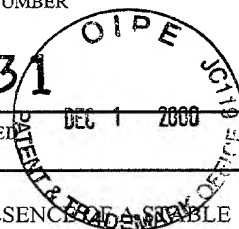


**TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)**

2988-661

09/701831



INTERNATIONAL APPLICATION NO.  
PCT/FR99/01272

INTERNATIONAL FILING DATE  
May 31, 1999

PRIORITY DATE CLAIMED  
June 3, 1998

TITLE OF INVENTION  
SHOCK VINYLAROMATIC POLYMER BY POLYMERIZATION OF A VINYLAROMATIC MONOMER IN THE PRESENCE OF A FREE RADICAL AND A POLYMERIZATION INITIATOR

APPLICANT(S) FOR DO/EO/US  
Jean-Marc BOUTILLIER

Applicant herewith submits to the United States Designated/ Elected Office (DO/EO/US) the following items under 35 U.S.C. 371:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the international Bureau).
  - b. ☒ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureaus.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 37(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)) (unexecuted).
10. ☒ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

**Items 11. to 16. below concern document(s) or information included:**

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.  
☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:

A copy of the PCT Request  
A copy of PCT publication with Search Report  
A copy of the revised Search Report  
A copy of the Preliminary Examination Report  
Copies of Notification of Registration Changes (form PCT/IB/306) (assignee's name change and attorney's address change)

INTERNATIONAL APPLICATION NO.  
PCT/FR99/01272

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INTERNATIONAL FILING DATE  
May 31, 1999

- 17.
- ☒
- The U.S. National Fee (35 U.S.C. 371(c)(1)) and other fees as follows:

CLAIMS				
(1)FOR	(2)NUMBER FILED	(3)NUMBER EXTRA	(4)RATE	(5)CALCULATIONS
TOTAL CLAIMS	47 - 20	22	X \$ 18.00	\$ 486.00
INDEPENDENT CLAIMS	2 - 3	0	X \$ 80.00	0.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$ 270.00	□
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)): <b>CHECK ONE BOX ONLY</b>				
□ International preliminary examination fee paid to USPTO (37 CFR 1.482)			\$ 690	
□ No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2))			\$ 710	
□ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO			\$1000	
□ International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2) to (4)			\$ 100	
<input checked="" type="checkbox"/> Filing with EPO or JPO search report			\$ 860	\$ 860.00
Surcharge of \$130.00 for furnishing the National fee or oath or declaration later than 20 □ 30 mos. from the earliest claimed priority date (37 CFR 1.492(e)).			\$	0.00
TOTAL OF ABOVE CALCULATIONS			=	1,346.00
Reduction by 1/2 for filing by small entity, if applicable. Affidavit must be filed also. (Note 37 CFR 1.9, 1.27, 1.28).			-	\$ 0.00
SUBTOTAL			=	1,346.00
Processing fee of \$130.00 for furnishing the English Translation later than 20 30 mos. from the earliest claimed priority date (37 CFR 1.492(f)).			+	
0			TOTAL FEES ENCLOSED	\$ 1,346.00

- a. ☐ A check in the amount of \$\_\_ to cover the above fees is enclosed.
- b. ☒ Please charge Deposit Account No. 16-1150 in the amount of \$1,346.00 to cover the above fees. A copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 16-1150. A copy of this sheet is enclosed.

- 18.
- ☒
- Other instructions
- 
- Please calculate the filing fee after entering the Preliminary Amendment.

- 19.
- ☒
- All correspondence for this application should be mailed to
- 
- PENNIE & EDMONDS LLP
- 
- 1155 AVENUE OF THE AMERICAS
- 
- NEW YORK, NEW YORK 10036-2711

- 20.
- ☒
- All telephone inquiries should be made to (212) 790-2803

Charles E. Miller  
NAME  
SIGNATURE24,576  
REGISTRATION NUMBERDecember 1, 2000  
DATE

EXPRESS MAIL NO.: EL 501 635 499 US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of: Boutiller

Serial No.: To be assigned

Group Art Unit: to be assigned

Filed: Concurrently filed

Examiner: to be assigned

For: PROCESS FOR THE  
PREPARATION OF  
THERMOPLASTIC MATERIALS

Attorney Docket No.: 2988-661

New York, NY  
December 1, 2000

PRELIMINARY AMENDMENT

Commissioner for Patents  
Washington, D.C. 20231

Sir:

Please enter the following amendments (changes are shown in bold-face for convenience for references) and remarks into the file of the present application. Applicant attached a clean form of amended claims as Appendix A.

IN CLAIMS:

Please amend claims 1 and 34 as follows:

1. (amended) Process for **[the preparation of] preparing** a composition **[comprising] of** a vinylaromatic polymer matrix surrounding rubber nodules, comprising **[a] the** step of polymerizing at least one vinylaromatic monomer in the presence of a rubber, **[of]** a stable free radical which is not introduced into the polymerization mixture in a form linked to the rubber, and **[of]** a polymerization initiator with a grafting character suitable for **[the]** said composition,  
**[- is such that in one of its sections at least 90% of the total area occupied by the nodules corresponds to capsules having an equivalent diameter ranging from 0.1 to 1  $\mu$ m, or else**  
**- is such that it comprises multi-occlusion-type nodules and is such that in one of its sections**

- 20 to 60% of the total area occupied by the particles corresponds to particles having an equivalent diameter ranging from 0.1 to 1  $\mu\text{m}$ ,

- 5 to 20% of the total area occupied by the particles corresponds to particles having an equivalent diameter ranging from 1 to 1.6  $\mu\text{m}$ , and

- 20 to 75% of the total area occupied by the particles corresponds to particles having an equivalent diameter of greater than 1.6  $\mu\text{m}$ .

the] said step being such that:

- if (SFR) represents the number of moles of stable free radical in the polymerization mixture,

- if  $F_{\text{SFR}}$  represents the functionality of the stable free radical, i.e. the number of sites on the same molecule of stable free radical having the stable free radical state,

- if (INIT) represents the number of moles of polymerization initiator in the polymerization mixture before phase inversion, and

- if  $F_{\text{INIT}}$  represents the functionality of the initiator introduced before phase inversion, i.e. the number of sites having the free radical state that each molecule of initiator is capable of generating, then:

$$0.05 < \frac{F_{\text{SFR}} \times (\text{SFR})}{F_{\text{INIT}} \times (\text{INIT})} < 1.$$

34. (amended) **A [Composition] composition comprising a vinylaromatic polymer matrix surrounding rubber nodules, [capable of being obtained by the process of claim 1]**

**- which is such that, in one of its sections, at least 90% of the total area is occupied by the nodules corresponds to capsules having an equivalent diameter ranging from 0.1 to 1  $\mu\text{m}$ , or alternatively**

**- which comprises multi-occlusion-type nodules and is such that in one of its sections**

- **20 to 60% of the total area is occupied by the particles corresponds to particles having an equivalent diameter ranging from 0.1 to 1  $\mu\text{m}$ ,**

- 5 to 20% of the total area is occupied by the particles corresponds to particles having an equivalent diameter ranging from 1 to 1.6  $\mu\text{m}$ , and
- 20 to 75% of the total area is occupied by the particles corresponds to particles having an equivalent diameter of greater than 1.6  $\mu\text{m}$ .

Please amend claims 2 -12, 14-19, 21-33, 35-36 and 39-41 as follows:

in claim 2, change "the previous claim" to --claim 1--;

in claims 3-11, 14, 22-29, 31-33 and 40, change "one of the preceding claims" to --claim 1--;

in claim 12, change "the preceding claim" to --claim 11--;

in claim 15, change "one of Claims 10 to 14" to --claim 10--;

in claim 16, change "one of Claims 10 to 15" to --claim 10--;

in claim 17, change "the preceding claim" to --claim 16--;

in claim 18, change "one of Claims 1 to 9" to --claim 1--;

in claim 19, change "the preceding claim" to --claim 18--;

in claim 21, change "the preceding claim" to --claim 20--;

in claim 30, change "the preceding claim" to --claim 29--;

in claim 35, change "the preceding claim or" to --claim 34--;

in claim 36, change "the preceding claim" to --claim 35--;

in claim 39, change "one of Claims 34 to 38" to --claim 34--;

in claim 40, change "the preceding claim" to --claim 39--; and

in claim 41, change "one of Claim 35 to 40" to --claim 35--.

### **REMARKS**


Claims 1-42 are pending. Claims have been amended to avoid multiply dependent claims. Applicants respectfully request that the amendments

and remarks made herein be entered and made of record in the file history of the present application.

No fee is believed to be due for this amendment. Should any fee be required, please charge same to Deposit Account No. 16-1150.

Respectfully submitted,

Date: December 1, 2000

  
\_\_\_\_\_  
Charles E. Miller 24,576  
(Reg. No.)

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IMPACT VINYLAROMATIC POLYMER  
BY POLYMERIZATION OF A VINYLAROMATIC MONOMER  
IN THE PRESENCE OF A STABLE FREE RADICAL  
AND OF A POLYMERIZATION INITIATOR

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The invention relates to a process for the preparation of an impact vinylaromatic composition, i.e. a composition comprising a vinylaromatic polymer matrix surrounding rubber nodules.

Patent Application EP 0,726,280 teaches that it is possible to produce an impact polystyrene by polymerizing a vinylaromatic monomer in the presence of a polybutadiene and of a stable free radical.

Patent EP 0,048,389 teaches that it is possible to obtain an impact polystyrene in which the nodules are essentially in the form of capsules, provided that a styrene-butadiene copolymer is used as the rubber.

The process according to the invention involves a step of polymerizing at least one vinylaromatic monomer in the presence of rubber, of a polymerization initiator and of a stable free radical, the said step being such that

- if (SFR) represents the number of moles of stable free radical in the polymerization mixture,
- if  $F_{SFR}$  represents the functionality of the stable free radical, i.e. the number of sites on the

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same molecule of stable free radical having the stable free radical state,

- if (INIT) represents the number of moles of polymerization initiator in the polymerization mixture,

5 and

- if  $F_{INIT}$  represents the functionality of the initiator, i.e. the number of sites having the free radical state that each molecule of initiator is capable of generating,

10 then:

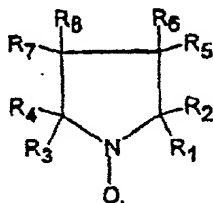
$$0.05 < \frac{F_{SFR} \times (SFR)}{F_{INIT} \times (INIT)} < 1,$$

and preferably:

$$0.05 < \frac{F_{SFR} \times (SFR)}{F_{INIT} \times (INIT)} < 0.5.$$

15

As an example of a stable free radical having a functionality  $F_{SFR}$  of 1, mention may be made of a molecule represented by:

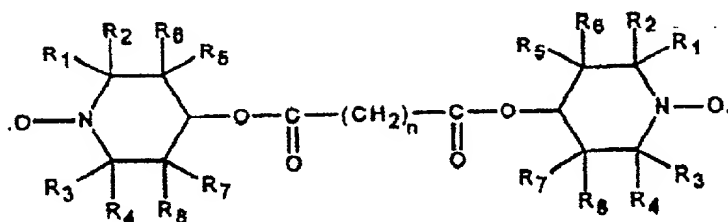


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in which the groups R1, R2, R3, R4, R5, R6, R7 and R8 represent alkyl radicals.



As an example of a stable free radical having a functionality  $F_{\text{SFR}}$  of 2, mention may be made of a molecule represented by:



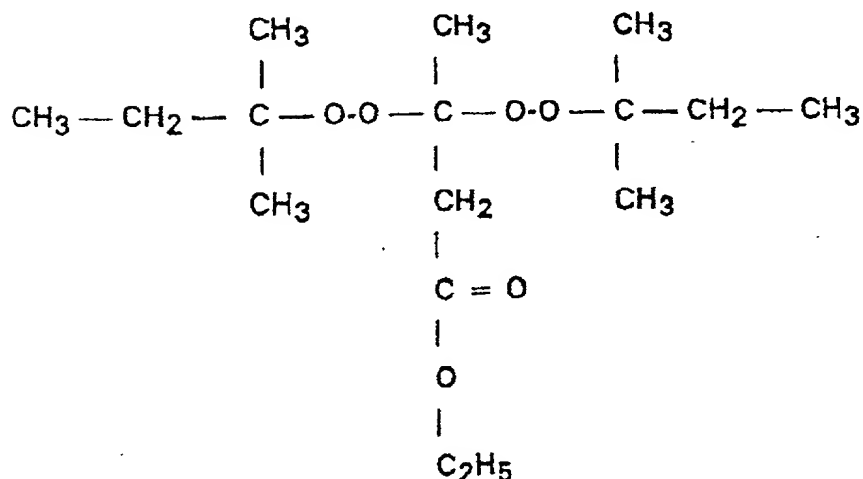
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in which the groups  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$  and  $R_8$  represent alkyl radicals and  $n$  represents a non-zero integer.

10

As an example of an initiator having a functionality  $F_{\text{INIT}}$  of 2, mention may be made of dicumyl peroxide.

As an example of an initiator having a functionality  $F_{\text{INIT}}$  of 4, mention may be made of ethyl-  
 15 3,3-di(*tert*-amylperoxy)butyrate which may be represented by:



as it contains two -O-O-links each capable of  
generating two sites having the free radical state,

5 namely -O<sup>•</sup>.

Using one particular  $[F_{\text{SFR}} \times (\text{SFR})] / [F_{\text{INIT}} \times$   
(INIT)] ratio, a polymerization range is defined within  
which it is possible to control and choose the  
morphology and the distribution of the sizes of nodules  
10 in the impact composition.

In addition, the process according to the  
invention is rapid, despite the use of a stable free  
radical which generally tends to slow down the  
polymerization.

15 The following morphologies of rubber nodules  
may be obtained:

- the "salami"-type morphology, which means  
that the rubber particle contains several generally  
approximately spherical, but non-concentric,  
20 vinylaromatic polymer occlusions;

- the "labyrinth"-type morphology, which means that the rubber particle contains several elongate, curved, generally non-spherical and generally unsymmetrical vinylaromatic polymer occlusions;

5           - the "onion"-type morphology, which means that the rubber particle is approximately spherical and contains, concentrically with respect to itself, several vinylaromatic polymer occlusions contained one within another; and

10           - the "capsule"-type morphology, which means that the generally approximately spherical rubber particle contains a single vinylaromatic polymer occlusion.

          The "salami", "labyrinth" and "onion"  
15 morphologies may be called "multi-occlusion" morphologies. In general, they are substantially coarser than the capsules.

          These morphologies in particular impinge on the impact properties and the gloss of the final  
20 compositions.

          When, for a given rubber and a given rubber content, the grafting is less, the nodules are essentially in salami form.

          Within the above-defined polymerization  
25 range, it is possible, for a given rubber and a given rubber content, to increase the proportion of nodules in labyrinth form, in onion form or in capsule form by increasing the grafting of the rubber.

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It is possible to further increase the proportion of nodules in capsule form by further increasing the grafting of the rubber. It is possible to promote the formation of capsules compared with the other morphologies by using a rubber of lower viscosity.

The advantages of the invention, in particular the possibility of obtaining a high proportion of nodules in labyrinth, onion or capsule form, or even a morphology essentially in capsule form, may be obtained from a rubber not comprising a polymerized vinylaromatic monomer unit and may be obtained by using a homopolybutadiene as the rubber.

The expression "grafting of the rubber" should be understood to mean the grafting of the rubber by the vinylaromatic monomer present in the polymerization mixture.

The grafting of the rubber may be increased by:

- using an initiator with a higher grafting power,
- increasing the polymerization temperature,
- increasing the amount of initiator.

The grafting power of the initiator may be determined by routine comparative tests by analysing the morphology induced by the nature of the initiator. The grafting power of the initiator is higher the more it tends to generate the following morphologies, given

in the direction of increasing grafting power: salami,  
then onion or labyrinth, then capsule. Very large  
amounts of initiator, for example so that the ratio of  
the product  $(INIT) \times F_{INIT}$  to the molar amount of  
5 vinylaromatic monomer is greater than  $2 \times 10^{-4}$ , or even  
greater than  $4 \times 10^{-4}$  or even greater than  $6 \times 10^{-4}$ , may  
be introduced. Such amounts are not usual in  
vinylaromatic monomer polymerization processes since  
they cause substantial heat generation, the heat being  
10 difficult to remove and possibly dangerous. In the  
context of the present invention, the Applicant has  
found that, on account of the amounts of initiator  
used, less heat was generated than normally observed.  
This phenomenon allows the use of large amounts of  
15 initiator, thereby allowing the grafting and the  
particle morphology to be controlled as desired.

The process according to the invention makes  
it possible to obtain particularly impact-resistant  
and/or particularly glossy compositions with a high  
20 polymerization rate.

The process according to the invention  
results in compositions having a high fluidity and a  
high Vicat softening point, combined with, if required,  
a high impact resistance.

25 If it is desired to produce a composition  
whose essential property is impact resistance  
(hereafter called "impact" composition), it is  
recommended to find conditions such that the rubber

nodules have partially both a salami and/or labyrinth  
 morphology and partially both an onion and/or capsule  
 morphology. In addition, it is recommended to find  
 conditions such that the nodule size distribution is  
 5 broad and even bimodal. In the context of the present  
 invention, when a composition at least partially  
 comprises salami- and/or labyrinth-type nodules and  
 when the grafting conditions are increased, an increase  
 in the amount of capsule-type nodules is observed and  
 10 the gloss of the composition is increased thereby.  
 Moreover, for this type of "impact" composition,  
 comprising salami- and/or labyrinth-type nodules, the  
 nodule size distribution is broader than for  
 compositions coming from the same process but in which  
 15 no stable free radical had been introduced. Such a  
 composition has a high impact resistance. For this type  
 of "impact" composition, the process according to the  
 invention allows good utilization of the rubber, that  
 is to say it leads to compositions having a high impact  
 20 resistance for a relatively small amount of rubber.

Such an "impact" composition is preferably  
 such that, in one of its sections,

- 20 to 60% of the total area occupied by the  
 particles corresponds to particles having an equivalent  
 25 diameter ranging from 0.1 to 1  $\mu\text{m}$ ,

- 5 to 20% of the total area occupied by the  
 particles corresponds to particles having an equivalent  
 diameter ranging from 1 to 1.6  $\mu\text{m}$  and

- 20 to 75% of the total area occupied by the particles corresponds to particles having an equivalent diameter of greater than 1.6  $\mu\text{m}$ .

When the grafting of the particles is relatively low, the morphology of the particles, as a function of the size range of the equivalent diameters, is as follows:

♦ 0.1 to 1  $\mu\text{m}$ : more than 95% of the particles have the salami or capsule morphology,

♦ 1 to 1.6  $\mu\text{m}$ : more than 95% of the particles have the salami morphology, and

♦ greater than 1.6  $\mu\text{m}$ : more than 95% of the particles have the salami morphology.

When the grafting of the particles is higher, the morphology of the particles, as a function of the size ranges, is as follows:

♦ 0.1 to 1  $\mu\text{m}$ : more than 95% of the particles have the capsule or onion or labyrinth morphology,

♦ 1 to 1.6  $\mu\text{m}$ : more than 95% of the particles have the onion or labyrinth morphology, and

♦ greater than 1.6  $\mu\text{m}$ : more than 95% of the particles have the labyrinth morphology.

The "impact" compositions may especially be used for producing injection-moulded articles in the audio-video field (cases for television sets or video recorders) or in the office field (cases for computers, printers or fax machines). In order to produce these articles, it is necessary to be able to have available

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compositions having a high fluidity (in order to facilitate injection moulding) together with a high impact resistance and a high Vicat softening temperature (in order to improve the hot strength, i.e. to limit heat-induced deformation). The invention makes it possible to obtain compositions having these combinations of properties.

The process according to the invention may also result in a composition in which the rubber nodules are essentially in capsule form. Such a composition (hereafter called "glossy" composition) has a high gloss and is, in general, essentially monomodal. Such a composition may be obtained by causing a high level of grafting during the polymerization and by using a rubber of sufficiently low viscosity. It is also important to take care that the stirring during the polymerization exerts sufficient shear for the capsule morphology to be obtained. Such a "glossy" composition is such that, in one of its cuts, at least 90% of the total area occupied by the particles corresponds to capsules having an equivalent diameter ranging from 0.1 to 1  $\mu\text{m}$ .

The "glossy" compositions also have good transparency, this being manifested by low haze values. Very low haze values may be obtained despite the use of a homopolybutadiene, whereas in the prior art it is general to use, as rubber, a styrene-butadiene copolymer in order to lower the haze. If required, so

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as to increase the transparency further, it is possible to blend these "glossy" compositions with crystal polystyrene. These glossy compositions, which may or may not be alloyed with crystal polystyrene, are used in particular in the packaging field for the manufacture, by thermoforming, of pots, goblets and trays, the average wall thickness of which is generally between 25 and 750 microns and more particularly between 50 and 250 microns.

In all cases, especially in that of the "impact" and "glossy" compositions, the final composition comprises a matrix of a vinylaromatic polymer surrounding particles of a rubber, the said composition also comprising a stable free radical and/or a stable-free-radical-generating group forming part of a polymer chain. In fact, the stable free radical may essentially be in a free form and/or in a form bound to a polymer chain by a covalent bond. In general, the tendency of a stable-free-radical-generating group to release its stable free radical increases with temperature. The final composition therefore has a higher or lower content of stable free radicals or stable-free-radical-generating groups depending on the intensity of the devolatilization treatment carried out on the said composition and also depending on the nature of the stable free radical or of the stable-free-radical-generating group. The devolatilization treatment is more intense the longer

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its duration and/or the higher its temperature and/or the higher its vacuum.

Because of the presence of a stable free radical and/or a stable-free-radical-generating group, the final composition has an improved resistance to hot depolymerization and to ultraviolet.

In addition, because of the possibility of using large amounts of polymerization initiator, especially of the peroxide family, the grafting of the rubber by the vinylaromatic monomer is improved, this having the effect, for a given temperature, of reducing the shrinkage of the material. This improvement produces a reduction in the burning rate of the material, something which is an appreciable advantage, especially in the audio-video field or the office field.

The rubber may, for example, have a viscosity as a 5% by weight solution in styrene, measured at 25°C, ranging from 15 to 300 mPa.s.

The rubber, especially in the case of a polybutadiene, generally has a weight-average molecular mass ( $M_w$ ), expressed in g/mol, ranging from 110,000 to 350,000, and preferably from 150,000 to 300,000, and generally has a number-average molecular mass ( $M_n$ ), expressed in g/mol, ranging from 50,000 to 250,000 and preferably from 70,000 to 200,000.

By way of example, for the case in which it is desired to produce an "impact" composition, i.e. one

comprising partially both nodules with the salami  
and/or labyrinth morphology and partially both nodules  
with the onion and/or capsule morphology, it is  
possible to use a homopolybutadiene having a viscosity  
5 as a 5% by weight solution in styrene, measured at  
25°C, ranging from 60 to 300 mPa.s. In the case of such  
an "impact" composition, the rubber, especially in the  
case of a polybutadiene, preferably has a weight-  
average molecular mass ranging from 175,000 to 350,000  
10 and even more preferably from 200,000 to 300,000, and  
preferably has a number-average molecular mass ranging  
from 70,000 to 250,000 and even more preferably from  
90,000 to 200,000.

By way of example, in the case in which it is  
15 desired to produce a "glossy" composition, i.e. one in  
which most of the nodules are in capsule form, it is  
possible to use a homopolybutadiene having a viscosity  
ranging from 15 to 60 mPa.s, measured at 25°C, as a 5%  
by weight solution in styrene. In the case of such a  
20 "glossy" composition, the rubber, especially in the  
case of a polybutadiene, preferably has a weight-  
average molecular mass ranging from 110,000 to 200,000  
and preferably ranging from 150,000 to 200,000, and  
preferably has a number-average molecular mass ranging  
25 from 50,000 to 200,000 and even more preferably from  
70,000 to 150,000.

A stable free radical should not be confused  
with free radicals whose lifetime is ephemeral (a few

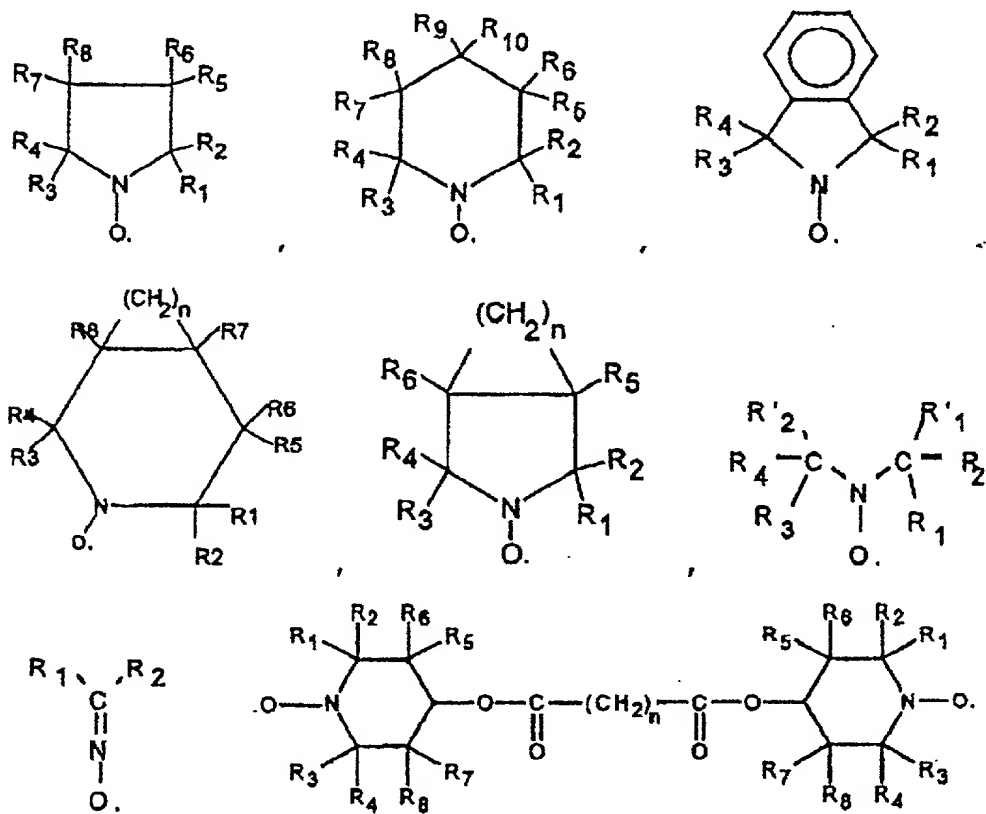
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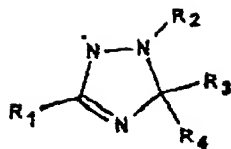
milliseconds), such as the free radicals produced by the usual polymerization initiators such as peroxides, hydroperoxides and azo-type initiators. Polymerization-initiating free radicals tend to accelerate the polymerization. By contrast, stable free radicals generally tend to slow down the polymerization. In general, it may be stated that a free radical is stable in the sense of the present invention if it is not a polymerization initiator and if, under the conditions of use of the present invention, the average lifetime of the radical is at least five minutes. Over this average lifetime, the molecules of the stable free radical continually alternate between the state of a radical and the state of a group bound to a polymer chain by a covalent bond. Of course, it is preferable for the stable free radical to exhibit good stability throughout the duration of its use in the context of the present invention. Generally speaking, a stable free radical may be isolated in the radical state at room temperature. A stable free radical is stable enough for its free radical state to be characterized using spectroscopic methods.

It will be recalled that the notion of a stable free radical is known by those skilled in the art for denoting a radical that is so persistent and unreactive with respect to air and to moisture in the ambient air that the pure radical may be handled and stored without any more precautions at room temperature

than those for most commercial chemicals (see, on the subject D. Griller and K. Ingold, Accounts of Chemical Research, 1976, 9, 13-19 or A. Forrester et al., Organic Chemistry of Stable Free Radicals, Academic Press, 1968).

The family of stable free radicals includes in particular the compounds acting as radical polymerization inhibitors for storing monomers, stable nitroxyl radicals, i.e. those comprising the =N-O<sup>•</sup> group. It is possible to use, as stable free radical, the radicals represented, for example, by the following formulae:





in which  $n$  represents a non-zero integer and  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R'_1$  and  $R'_2$ , which may be identical or  
 5 different, represent a halogen atom, such as a chlorine, bromine or iodine atom, a saturated or unsaturated, linear, branched or cyclic hydrocarbon group, such as an alkyl or phenyl radical, or an ester group  $-COOR$  or an alkoxy group  $-OR$ , or a phosphonate  
 10 group  $-PO(OR)_2$ , or a polymer chain which may, for example, be a polymethyl methacrylate, polybutadiene or polyolefin, such as polyethylene or polypropylene, chain but which is preferably a polystyrene chain, and in which  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$  and  $R_{10}$ , which may be  
 15 identical or different, may be chosen from the same family of groups as that which was envisaged for  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R'_1$  and  $R'_2$  and may also represent a hydrogen atom, a hydroxide group  $-OH$ , an acid group such as  $-COOH$  or  $-PO(OH)_2$  or  $-SO_3H$ .

20 In particular, the stable free radical may be 2,2,5,5-tetramethyl-1-pyrrolidinyloxy sold under the name PROXYL, 2,2,6,6-tetramethyl-1-piperidinyloxy, generally sold under the name TEMPO, 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy sold under the name 4-  
 25 hydroxy TEMPO, or bis(1-oxy-2,2,6,6-

tetramethylpiperidin-4-yl)sebacate sold under the brand CXA 5415 by the company Ciba Specialty Chemical.

The stable free radical may also be chosen from the following list:

- 5                   - N-tert-butyl-1-phenyl-2-methylpropyl  
nitroxide,
- N-tert-butyl-1-(2-naphthyl)-2-methylpropyl  
nitroxide,
- N-tert-butyl-1-diethylphosphono-2,2-  
10 dimethylpropyl nitroxide,
- N-tert-butyl-1-dibenzylphosphono-2,2-  
dimethylpropyl nitroxide,
- N-phenyl-1-diethylphosphono-2,2-dimethyl-  
propyl nitroxide,
- 15                  - N-phenyl-1-diethylphosphono-1-methylethyl  
nitroxide,
- N-(1-phenyl-2-methylpropyl)-1-  
diethylphosphono-1-methylethyl nitroxide
- 4-oxo-2,2,6,6-tetramethyl-1-piperidinyloxy,
- 20                  - 2,4,6-tri-tert-butylphenoxy.

In the context of the present application, the stable free radical is not introduced into the polymerization mixture in a form bound to the rubber, as would be the case with a rubber carrying a stable-  
25 free-radical-generating group.

The initiator is a radical polymerization initiator which may be chosen from diacyl peroxides,

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peroxyesters, dialkyl peroxides and peroxyacetals.

Particularly suitable initiators are the following:

- isopropyl *tert*-butyl peroxy carbonate,
- 2-ethylhexyl *tert*-butyl peroxy carbonate,
- 5 - dicumyl peroxide
- di-*tert*-butyl peroxide,
- 1,1-bis(*tert*-butylperoxy)cyclohexane,
- 1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane,
- 10 - *tert*-butyl peroxyacetate,
- cumyl *tert*-butyl peroxide,
- *tert*-butyl perbenzoate,
- *tert*-butyl per-2-ethylhexanoate,
- 2,2-bis(*tert*-butylperoxy)butane,
- 15 - butyl 4,4-bis(*tert*-butyl)valerate,
- ethyl 3,3-bis(*tert*-butyl)butyrate,
- 2,2-bis(4,4-di-*tert*-butylperoxycyclohexyl)propane.

The initiators which generate at least one  
 20 *tert*-butyloxy radical, i.e.  $(\text{CH}_3)_3\text{C}-\text{O}^\cdot$ , are more particularly suitable.

It is preferable to choose a radical-generating initiator having the least possible tendency to form an adduct with the stable free radical, the  
 25 said radicals furthermore having the highest possible potential of grafting onto the rubber by pulling off hydrogen atoms from the said rubber.



The term "vinylaromatic monomer" in the context of the present invention should be understood to mean an ethylenically unsaturated aromatic monomer such as styrene, vinyltoluene, alphas-methyl styrene, 5 alphaethyl styrene, 4-methyl styrene, 3-methyl styrene, 4-methoxy styrene, 2-hydroxymethyl styrene, 4-ethyl styrene, 4-ethoxy styrene, 3,4-dimethyl styrene, 2-chloro styrene, 3-chloro styrene, 4-chloro-3-methyl styrene, 3-*tert*-butyl styrene, 2,4-dichloro styrene, 10 2,6-dichloro styrene, 1-vinylnaphthalene and vinylanthracene.

Styrene is a preferred vinylaromatic monomer.

The rubber is an elastomer normally used for imparting impact properties to vinylaromatic polymers. 15 The rubber may be a conjugated polydiene, such as polybutadiene, polyisoprene and styrene-butadiene copolymers of the elastomer type, also called SBR (styrene-butadiene rubber). The rubber may comprise less than 10% and preferably less than 5% by weight of 20 a polymerized vinylaromatic monomer unit. The rubber may not comprise a vinylaromatic monomer as a polymerization unit, as is the case for styrene-butadiene block copolymers. The rubber may therefore be a homopolybutadiene. The polymerization mixture during 25 the step of the process according to the invention may initially comprise:

- per 100 parts by weight of vinylaromatic monomer,

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- 2 to 35 parts by weight of rubber and
- 0 to 50 parts by weight of solvent.

The solvent may be organic and chosen so that it does not boil under the polymerization conditions and in such a way that it is miscible with the vinylaromatic monomer and with the vinylaromatic polymer derived therefrom. It is possible to use alicyclic hydrocarbons such as cyclohexane, or preferably aromatics, such as toluene, benzene, ethylbenzene or xylene.

The polymerization mixture may also contain at least one monomer copolymerizable with the vinylaromatic monomer or monomers, such as, for example at least one acrylic or methacrylic monomer or acrylonitrile. The term "polymerization" therefore covers those of homopolymerization, copolymerization and interpolymerization and the term "polymer" covers those of homopolymer, copolymer and interpolymer.

After the so-called phase-inversion phenomenon, i.e. the formation of particles, it is possible to add a polymerization initiator identical to or different from that present at the start of polymerization, so as to increase the polymerization rate. The amounts of initiator added after phase inversion are not to be taken into account in the calculation of the  $[F_{SFR} \times (SFR)]/[F_{INIT} \times (INIT)]$  ratio with which the present application is concerned.

Preferably, the weight-average molecular mass ( $M_w$ ) of the vinylaromatic polymer matrix ranges from 90,000 to 250,000 and preferably from 100,000 to 200,000. Generally, the polydispersivity  $M_w/M_n$  of the matrix ranges from 2.2 to 3.5 and more particularly from 2.3 to 3.

In the case of an "impact" composition, the weight-average molecular mass of the matrix generally ranges from 90,000, to 200,000 and preferably from 100,000 to 150,000, for example from 110,000 to 130,000.

In the case of a "glossy" composition, the weight-average molecular mass of the matrix generally ranges from 130,000 to 250,000, for example from 150,000 to 200,000.

It is possible to add to the polymerization mixture, before or during the polymerization, at least one additive normally used in this kind of preparation. These additives may be plasticizers, such as mineral oils, butyl stearate or dioctyl phthalate, or stabilizers, such as antioxidants, which may be phenol substituted with an alkyl group, such as di-tert-butylparacresol, or phosphites such as trinonylphenyl phosphite.

If a plasticizer is introduced, this may be so in an amount such that it is present in the finally synthesized composition in an amount of 0 to 6% by weight.

If a stabilizer is introduced, this may be present in the polymerization mixture in an amount of 0 to 3000 ppm.

During the polymerization, the well-known  
5 phenomenon of phase inversion occurs, which leads to the formation of rubber nodules dispersed in a vinylaromatic polymer matrix. During this polymerization, the stirring must be vigorous enough for the dispersion of the rubber nodules to be uniform.

10 The polymerization may be carried out in batch mode. The polymerization may also be carried out continuously and, in this case, preferably so that the phase inversion takes place in a plug-flow reactor. If the polymerization is carried out continuously so that  
15 the phase inversion takes place in a continuously stirred tank reactor or CSTR, then preferably the polymerization was already started in at least one other reactor before entry into the said phase-inversion continuously stirred tank reactor.

20 After polymerization, it is expedient to eliminate the volatile species such as the monomers that have not reacted, and any organic solvent. This may be carried out using conventional techniques, such as by the use of a devolatilizer operating hot and  
25 under vacuum.

The final rubber and vinylaromatic polymer content of the composition according to the invention depends on the degree of conversion to which the

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polymerization has been taken before elimination of the volatile species. This is because if the degree of polymerization conversion is low, elimination of the volatile species will remove a large amount of vinylaromatic monomer and the final rubber content of the composition will be higher.

The polymerization conversion may be monitored using samples taken during the polymerization step and by determining the solids content on the samples taken. The term "solids content" should be understood to mean the percentage by weight of solids obtained after evaporation under a vacuum of 25 millibar for approximately 20 minutes at 200°C of the specimens taken with respect to the initial weight of the specimen taken. It may be possible to drive the polymerization, for example, until a solids content of between 60 and 80% by weight is obtained.

It is preferable to adjust the amounts of ingredients introduced and the manufacturing conditions so that the final composition contains between 2 and 25% and even more preferably between 4 and 15% of rubber.

Preferably, a step of the process according to the invention is at least partially carried out at a temperature ranging from 80 to 140°C, for example between 90 and 130°C.

Preferably, the step of the process according to the invention is carried out at least partially

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before phase inversion at a temperature T such that  
 $T_4 - 20^\circ\text{C} < T < T_4 + 20^\circ\text{C}$  and preferably such that  
 $T_4 - 10^\circ\text{C} < T < T_4 + 10^\circ\text{C}$ , in which  $T_4$  represents the  
 temperature at which 50% of the initiator has  
 5 decomposed in one hour. Most of the polymerization may  
 be carried out in the temperature ranges just given.

The polymerization initiator may, for  
 example, be present so that the molar ratio of (INIT)  $\times$   
 $F_{\text{INIT}}$  to the amount of vinylaromatic monomer goes from  
 10  $1 \times 10^{-5}$  to  $1 \times 10^{-2}$ .

Preferably, the stable free radical is  
 present so that

$$0.1 < \frac{(\text{SFR}) \times F_{\text{SFR}}}{(\text{RU})} < 10$$

15

in which (RU) represents the number of moles of rubber.

The polymerization process according to the  
 invention makes it possible to obtain "impact"  
 compositions having both a high fluidity (high  $MI_2$ ), a  
 20 high impact resistance and a high Vicat softening  
 point. It is generally very difficult to obtain high  
 values for these three properties at the same time.

In order to increase the fluidity, the  
 molecular mass of the vinylaromatic polymer should be  
 25 decreased, which may be achieved by increasing the  
 polymerization temperature and by decreasing the  
 polymerization time, and/or by increasing the  
 concentration of chain-transfer agent (for example a

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mercaptan, such as n-dodecyl mercaptan or tert-dodecyl mercaptan) in the polymerization mixture, preferably after phase inversion. In the context of the process according to the invention, it is possible, using the means just mentioned, to obtain an "impact" composition having a melt index MI<sub>5</sub> (210°C/5 kg) of greater than 15, while still maintaining a Vicat softening temperature (1 kg) of greater than 94, or even greater than 94.5, and a notched Izod impact strength of greater than 8, or even greater than 9.

In the examples which follow, the following technical terms have been used:

- melt index MI<sub>5</sub> (at 210°C/5 kg): ISO 1133 H standard,
- notched Izod impact strength: ISO 180/1A standard,
- Vicat softening temperature (1 kg): ISO 306A50 standard,
- gloss: this is measured on samples 60 mm in diameter, by determining the reflected light when the specimen is exposed to a light beam at an angle of 60°, according to the ASTM D523 standard. The measurement apparatus used is a Byk Gardner Micro-Tri-Gloss GLØ1 machine,
- haze: this is measured on a film approximately 300 microns in thickness, obtained by hot compression of an injection-moulded sample 60 mm in diameter and 2 mm in thickness. It is measured using a

TABLE 1	
Summary of the results of the 1990-1991 survey of the health status of the population of the Republic of Serbia	
1. General characteristics of the population	
1.1. Total population	10,000,000
1.2. Urban population	6,000,000
1.3. Rural population	4,000,000
1.4. Population density	100/km <sup>2</sup>
1.5. Life expectancy at birth	75 years
1.6. Infant mortality rate	10/1,000 live births
1.7. Fertility rate	1.5 children per woman
1.8. Sex ratio	100 males per 100 females
1.9. Ethnic composition	90% Serbs, 10% others
1.10. Religion	90% Orthodox, 10% others
1.11. Education level	90% primary, 10% secondary
1.12. Employment status	50% employed, 50% unemployed
1.13. Income level	Low
1.14. Housing conditions	Basic
1.15. Access to health services	Good
1.16. Access to education	Good
1.17. Access to social services	Good
1.18. Access to culture and recreation	Good
1.19. Access to information	Good
1.20. Access to transport	Good
1.21. Access to food	Good
1.22. Access to clothing	Good
1.23. Access to housing	Good
1.24. Access to water supply	Good
1.25. Access to sewerage	Good
1.26. Access to electricity	Good
1.27. Access to telephone	Good
1.28. Access to internet	Good
1.29. Access to mobile phone	Good
1.30. Access to car	Good
1.31. Access to bicycle	Good
1.32. Access to motorcycle	Good
1.33. Access to boat	Good
1.34. Access to plane	Good
1.35. Access to train	Good
1.36. Access to bus	Good
1.37. Access to taxi	Good
1.38. Access to private car	Good
1.39. Access to private bus	Good
1.40. Access to private train	Good
1.41. Access to private plane	Good
1.42. Access to private boat	Good
1.43. Access to private motorcycle	Good
1.44. Access to private bicycle	Good
1.45. Access to private motorcycle	Good
1.46. Access to private boat	Good
1.47. Access to private plane	Good
1.48. Access to private boat	Good
1.49. Access to private plane	Good
1.50. Access to private boat	Good
1.51. Access to private plane	Good
1.52. Access to private boat	Good
1.53. Access to private plane	Good
1.54. Access to private boat	Good
1.55. Access to private plane	Good
1.56. Access to private boat	Good
1.57. Access to private plane	Good
1.58. Access to private boat	Good
1.59. Access to private plane	Good
1.60. Access to private boat	Good
1.61. Access to private plane	Good
1.62. Access to private boat	Good
1.63. Access to private plane	Good
1.64. Access to private boat	Good
1.65. Access to private plane	Good
1.66. Access to private boat	Good
1.67. Access to private plane	Good
1.68. Access to private boat	Good
1.69. Access to private plane	Good
1.70. Access to private boat	Good
1.71. Access to private plane	Good
1.72. Access to private boat	Good
1.73. Access to private plane	Good
1.74. Access to private boat	Good
1.75. Access to private plane	Good
1.76. Access to private boat	Good
1.77. Access to private plane	Good
1.78. Access to private boat	Good
1.79. Access to private plane	Good
1.80. Access to private boat	Good
1.81. Access to private plane	Good
1.82. Access to private boat	Good
1.83. Access to private plane	Good
1.84. Access to private boat	Good
1.85. Access to private plane	Good
1.86. Access to private boat	Good
1.87. Access to private plane	Good
1.88. Access to private boat	Good
1.89. Access to private plane	Good
1.90. Access to private boat	Good
1.91. Access to private plane	Good
1.92. Access to private boat	Good
1.93. Access to private plane	Good
1.94. Access to private boat	Good
1.95. Access to private plane	Good
1.96. Access to private boat	Good
1.97. Access to private plane	Good
1.98. Access to private boat	Good
1.99. Access to private plane	Good
1.100. Access to private boat	Good

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1. General characteristics of the population	
1.1. Total population	10,000,000
1.2. Urban population	5,500,000
1.3. Rural population	4,500,000
1.4. Population density	100/km <sup>2</sup>
1.5. Life expectancy at birth	75 years
1.6. Infant mortality rate	10/1,000 live births
1.7. Fertility rate	1.5 children per woman
2. Health status of the population	
2.1. Prevalence of chronic diseases	15%
2.2. Prevalence of acute diseases	5%
2.3. Prevalence of mental disorders	2%
2.4. Prevalence of disabilities	3%
2.5. Prevalence of smoking	25%
2.6. Prevalence of alcohol consumption	10%
2.7. Prevalence of drug use	1%
2.8. Prevalence of physical activity	15%
2.9. Prevalence of diet-related diseases	10%
2.10. Prevalence of infectious diseases	5%
2.11. Prevalence of non-infectious diseases	10%
2.12. Prevalence of congenital diseases	1%
2.13. Prevalence of acquired diseases	1%
2.14. Prevalence of autoimmune diseases	1%
2.15. Prevalence of endocrine diseases	1%
2.16. Prevalence of musculoskeletal diseases	1%
2.17. Prevalence of neurological diseases	1%
2.18. Prevalence of psychiatric diseases	1%
2.19. Prevalence of dermatological diseases	1%
2.20. Prevalence of ophthalmological diseases	1%
2.21. Prevalence of otolaryngological diseases	1%
2.22. Prevalence of urological diseases	1%
2.23. Prevalence of gynecological diseases	1%
2.24. Prevalence of pediatric diseases	1%
2.25. Prevalence of geriatric diseases	1%
2.26. Prevalence of diseases of the elderly	1%
2.27. Prevalence of diseases of the young	1%
2.28. Prevalence of diseases of the middle-aged	1%
2.29. Prevalence of diseases of the adult	1%
2.30. Prevalence of diseases of the child	1%
2.31. Prevalence of diseases of the infant	1%
2.32. Prevalence of diseases of the neonate	1%
2.33. Prevalence of diseases of the fetus	1%
2.34. Prevalence of diseases of the embryo	1%
2.35. Prevalence of diseases of the zygote	1%
2.36. Prevalence of diseases of the blastocyst	1%
2.37. Prevalence of diseases of the germ cell	1%
2.38. Prevalence of diseases of the somatic cell	1%
2.39. Prevalence of diseases of the stem cell	1%
2.40. Prevalence of diseases of the progenitor cell	1%
2.41. Prevalence of diseases of the mature cell	1%
2.42. Prevalence of diseases of the differentiated cell	1%
2.43. Prevalence of diseases of the specialized cell	1%
2.44. Prevalence of diseases of the functional cell	1%
2.45. Prevalence of diseases of the structural cell	1%
2.46. Prevalence of diseases of the cellular component	1%
2.47. Prevalence of diseases of the tissue component	1%
2.48. Prevalence of diseases of the organ component	1%
2.49. Prevalence of diseases of the system component	1%
2.50. Prevalence of diseases of the organism component	1%
2.51. Prevalence of diseases of the individual component	1%
2.52. Prevalence of diseases of the population component	1%
2.53. Prevalence of diseases of the community component	1%
2.54. Prevalence of diseases of the society component	1%
2.55. Prevalence of diseases of the culture component	1%
2.56. Prevalence of diseases of the civilization component	1%
2.57. Prevalence of diseases of the modern component	1%
2.58. Prevalence of diseases of the post-modern component	1%
2.59. Prevalence of diseases of the global component	1%
2.60. Prevalence of diseases of the universal component	1%
2.61. Prevalence of diseases of the eternal component	1%
2.62. Prevalence of diseases of the infinite component	1%
2.63. Prevalence of diseases of the boundless component	1%
2.64. Prevalence of diseases of the immeasurable component	1%
2.65. Prevalence of diseases of the incalculable component	1%
2.66. Prevalence of diseases of the innumerable component	1%
2.67. Prevalence of diseases of the uncountable component	1%
2.68. Prevalence of diseases of the unmeasurable component	1%
2.69. Prevalence of diseases of the unquantifiable component	1%
2.70. Prevalence of diseases of the unassessable component	1%
2.71. Prevalence of diseases of the uncalculable component	1%
2.72. Prevalence of diseases of the uncomputable component	1%
2.73. Prevalence of diseases of the unestimable component	1%
2.74. Prevalence of diseases of the unguessable component	1%
2.75. Prevalence of diseases of the unpredictable component	1%
2.76. Prevalence of diseases of the unforeseeable component	1%
2.77. Prevalence of diseases of the unpreventable component	1%
2.78. Prevalence of diseases of the unavoidable component	1%
2.79. Prevalence of diseases of the inescapable component	1%
2.80. Prevalence of diseases of the inevitable component	1%
2.81. Prevalence of diseases of the ineluctable component	1%
2.82. Prevalence of diseases of the inescapable component	1%
2.83. Prevalence of diseases of the inevitable component	1%
2.84. Prevalence of diseases of the ineluctable component	1%
2.85. Prevalence of diseases of the inescapable component	1%
2.86. Prevalence of diseases of the inevitable component	1%
2.87. Prevalence of diseases of the ineluctable component	1%
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2.94. Prevalence of diseases of the inescapable component	1%
2.95. Prevalence of diseases of the inevitable component	1%
2.96. Prevalence of diseases of the ineluctable component	1%
2.97. Prevalence of diseases of the inescapable component	1%
2.98. Prevalence of diseases of the inevitable component	1%
2.99. Prevalence of diseases of the ineluctable component	1%
2.100. Prevalence of diseases of the inescapable component	1%

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1.2. Urban population	6,000,000
1.3. Rural population	4,000,000
1.4. Population density	100/km <sup>2</sup>
1.5. Life expectancy at birth	75 years
1.6. Infant mortality rate	10/1,000 live births
1.7. Fertility rate	1.5 children per woman
1.8. Sex ratio	100 males per 100 females
1.9. Ethnic composition	90% Serbs, 10% others
1.10. Religion	90% Orthodox, 10% others
1.11. Education level	90% primary, 10% secondary
1.12. Employment status	50% employed, 50% unemployed
1.13. Income level	Low
1.14. Housing conditions	Basic
1.15. Access to health services	Good
1.16. Environmental quality	Good
1.17. Social stability	Good
1.18. Political system	Democratic
1.19. Legal system	Sound
1.20. Cultural heritage	Rich
1.21. Sports facilities	Good
1.22. Recreation facilities	Good
1.23. Transportation facilities	Good
1.24. Communication facilities	Good
1.25. Information facilities	Good
1.26. Social services	Good
1.27. Public services	Good
1.28. Private services	Good
1.29. Voluntary services	Good
1.30. Community services	Good
1.31. Family services	Good
1.32. Child services	Good
1.33. Elderly services	Good
1.34. Disability services	Good
1.35. Mental health services	Good
1.36. Substance abuse services	Good
1.37. HIV/AIDS services	Good
1.38. Tuberculosis services	Good
1.39. Malaria services	Good
1.40. Dengue fever services	Good
1.41. Typhoid fever services	Good
1.42. Cholera services	Good
1.43. Shigellosis services	Good
1.44. Giardiasis services	Good
1.45. Cryptosporidiosis services	Good
1.46. Toxoplasmosis services	Good
1.47. Cysticercosis services	Good
1.48. Echinococcosis services	Good
1.49. Brucellosis services	Good
1.50. Rabies services	Good
1.51. Anthrax services	Good
1.52. Botulism services	Good
1.53. Tetanus services	Good
1.54. Diphtheria services	Good
1.55. Pertussis services	Good
1.56. Measles services	Good
1.57. Mumps services	Good
1.58. Rubella services	Good
1.59. Varicella services	Good
1.60. Herpes services	Good
1.61. HIV services	Good
1.62. AIDS services	Good
1.63. Tuberculosis services	Good
1.64. Malaria services	Good
1.65. Dengue fever services	Good
1.66. Typhoid fever services	Good
1.67. Shigellosis services	Good
1.68. Giardiasis services	Good
1.69. Cryptosporidiosis services	Good
1.70. Toxoplasmosis services	Good
1.71. Cysticercosis services	Good
1.72. Echinococcosis services	Good
1.73. Brucellosis services	Good
1.74. Rabies services	Good
1.75. Anthrax services	Good
1.76. Botulism services	Good
1.77. Tetanus services	Good
1.78. Diphtheria services	Good
1.79. Pertussis services	Good
1.80. Measles services	Good
1.81. Mumps services	Good
1.82. Rubella services	Good
1.83. Varicella services	Good
1.84. Herpes services	Good
1.85. HIV services	Good
1.86. AIDS services	Good
1.87. Tuberculosis services	Good
1.88. Malaria services	Good
1.89. Dengue fever services	Good
1.90. Typhoid fever services	Good
1.91. Shigellosis services	Good
1.92. Giardiasis services	Good
1.93. Cryptosporidiosis services	Good
1.94. Toxoplasmosis services	Good
1.95. Cysticercosis services	Good
1.96. Echinococcosis services	Good
1.97. Brucellosis services	Good
1.98. Rabies services	Good
1.99. Anthrax services	Good
1.100. Botulism services	Good

TABLE 1	
Summary of the results of the 1990-1991 survey of the health status of the population of the Republic of Serbia	
1. Demographic data	
Population (1991)	10,000,000
Population (1981)	9,000,000
Population (1971)	8,000,000
Population (1961)	7,000,000
Population (1951)	6,000,000
Population (1941)	5,000,000
Population (1931)	4,000,000
Population (1921)	3,000,000
Population (1911)	2,000,000
Population (1901)	1,000,000
Population (1891)	1,000,000
Population (1881)	1,000,000
Population (1871)	1,000,000
Population (1861)	1,000,000
Population (1851)	1,000,000
Population (1841)	1,000,000
Population (1831)	1,000,000
Population (1821)	1,000,000
Population (1811)	1,000,000
Population (1801)	1,000,000
Population (1791)	1,000,000
Population (1781)	1,000,000
Population (1771)	1,000,000
Population (1761)	1,000,000
Population (1751)	1,000,000
Population (1741)	1,000,000
Population (1731)	1,000,000
Population (1721)	1,000,000
Population (1711)	1,000,000
Population (1701)	1,000,000
Population (1691)	1,000,000
Population (1681)	1,000,000
Population (1671)	1,000,000
Population (1661)	1,000,000
Population (1651)	1,000,000
Population (1641)	1,000,000
Population (1631)	1,000,000
Population (1621)	1,000,000
Population (1611)	1,000,000
Population (1601)	1,000,000
Population (1591)	1,000,000
Population (1581)	1,000,000
Population (1571)	1,000,000
Population (1561)	1,000,000
Population (1551)	1,000,000
Population (1541)	1,000,000
Population (1531)	1,000,000
Population (1521)	1,000,000
Population (1511)	1,000,000
Population (1501)	1,000,000
Population (1491)	1,000,000
Population (1481)	1,000,000
Population (1471)	1,000,000
Population (1461)	1,000,000
Population (1451)	1,000,000
Population (1441)	1,000,000
Population (1431)	1,000,000
Population (1421)	1,000,000
Population (1411)	1,000,000
Population (1401)	1,000,000
Population (1391)	1,000,000
Population (1381)	1,000,000
Population (1371)	1,000,000
Population (1361)	1,000,000
Population (1351)	1,000,000
Population (1341)	1,000,000
Population (1331)	1,000,000
Population (1321)	1,000,000
Population (1311)	1,000,000
Population (1301)	1,000,000
Population (1291)	1,000,000
Population (1281)	1,000,000
Population (1271)	1,000,000
Population (1261)	1,000,000
Population (1251)	1,000,000
Population (1241)	1,000,000
Population (1231)	1,000,000
Population (1221)	1,000,000
Population (1211)	1,000,000
Population (1201)	1,000,000
Population (1191)	1,000,000
Population (1181)	1,000,000
Population (1171)	1,000,000
Population (1161)	1,000,000
Population (1151)	1,000,000
Population (1141)	1,000,000
Population (1131)	1,000,000
Population (1121)	1,000,000
Population (1111)	1,000,000
Population (1101)	1,000,000
Population (1091)	1,000,000
Population (1081)	1,000,000
Population (1071)	1,000,000
Population (1061)	1,000,000
Population (1051)	1,000,000
Population (1041)	1,000,000
Population (1031)	1,000,000
Population (1021)	1,000,000
Population (1011)	1,000,000
Population (1001)	1,000,000
Population (991)	1,000,000
Population (981)	1,000,000
Population (971)	1,000,000
Population (961)	1,000,000
Population (951)	1,000,000
Population (941)	1,000,000
Population (931)	1,000,000
Population (921)	1,000,000
Population (911)	1,000,000
Population (901)	1,000,000
Population (891)	1,000,000
Population (881)	1,000,000
Population (871)	1,000,000
Population (861)	1,000,000
Population (851)	1,000,000
Population (841)	1,000,000
Population (831)	1,000,000
Population (821)	1,000,000

TABLE 1	
Summary of the results of the 1997-1998 survey of the prevalence of hepatitis B virus (HBV) infection in the adult population of the Republic of Serbia	
Region	
Belgrade	1.1%
Baranja	0.5%
Podunavlje	0.4%
Central Serbia	0.6%
South Serbia	0.3%
North Serbia	0.2%
West Serbia	0.1%
East Serbia	0.1%
Overall	0.5%
Gender	
Male	0.6%
Female	0.4%
Overall	0.5%
Age group	
15-24	0.1%
25-34	0.2%
35-44	0.3%
45-54	0.4%
55-64	0.5%
65-74	0.6%
75+	0.7%
Overall	0.5%
Education	
Primary	0.3%
Secondary	0.4%
University	0.6%
Overall	0.5%
Occupation	
Health care	0.8%
Education	0.6%
Government	0.5%
Private	0.4%
Overall	0.5%
Marital status	
Married	0.5%
Single	0.4%
Divorced	0.3%
Widowed	0.2%
Overall	0.5%
Family size	
1-2	0.3%
3-4	0.4%
5-6	0.5%
7-8	0.6%
9-10	0.7%
Overall	0.5%
Travel history	
Yes	0.6%
No	0.4%
Overall	0.5%
HBV infection	
HBsAg	0.5%
Anti-HBc	0.6%
Anti-HBe	0.4%
Overall	0.5%

TABLE 1	
Summary of the results of the 1990-1991 survey of the health status of the population of the Republic of Serbia	
1. General characteristics of the population	
1.1. Total population	10,000,000
1.2. Urban population	6,000,000
1.3. Rural population	4,000,000
1.4. Population density	100/km <sup>2</sup>
1.5. Life expectancy at birth	75 years
1.6. Infant mortality rate	10/1,000 live births
1.7. Fertility rate	1.5 children per woman
1.8. Sex ratio	100 males per 100 females
1.9. Ethnic composition	90% Serbs, 10% others
1.10. Religion	90% Orthodox, 10% others
1.11. Education level	90% primary, 10% secondary
1.12. Employment status	50% employed, 50% unemployed
1.13. Income level	Low
1.14. Housing conditions	Basic
1.15. Access to health services	Good
1.16. Environmental quality	Good
1.17. Social stability	Good
1.18. Political system	Democratic
1.19. Legal system	Sound
1.20. Cultural life	Rich
1.21. Sports participation	High
1.22. Leisure activities	Varied
1.23. Family structure	Traditional
1.24. Marriage rate	High
1.25. Divorce rate	Low
1.26. Fertility rate	1.5 children per woman
1.27. Infant mortality rate	10/1,000 live births
1.28. Life expectancy at birth	75 years
1.29. Sex ratio	100 males per 100 females
1.30. Ethnic composition	90% Serbs, 10% others
1.31. Religion	90% Orthodox, 10% others
1.32. Education level	90% primary, 10% secondary
1.33. Employment status	50% employed, 50% unemployed
1.34. Income level	Low
1.35. Housing conditions	Basic
1.36. Access to health services	Good
1.37. Environmental quality	Good
1.38. Social stability	Good
1.39. Political system	Democratic
1.40. Legal system	Sound
1.41. Cultural life	Rich
1.42. Sports participation	High
1.43. Leisure activities	Varied
1.44. Family structure	Traditional
1.45. Marriage rate	High
1.46. Divorce rate	Low
1.47. Fertility rate	1.5 children per woman
1.48. Infant mortality rate	10/1,000 live births
1.49. Life expectancy at birth	75 years
1.50. Sex ratio	100 males per 100 females
1.51. Ethnic composition	90% Serbs, 10% others
1.52. Religion	90% Orthodox, 10% others
1.53. Education level	90% primary, 10% secondary
1.54. Employment status	50% employed, 50% unemployed
1.55. Income level	Low
1.56. Housing conditions	Basic
1.57. Access to health services	Good
1.58. Environmental quality	Good
1.59. Social stability	Good
1.60. Political system	Democratic
1.61. Legal system	Sound
1.62. Cultural life	Rich
1.63. Sports participation	High
1.64. Leisure activities	Varied
1.65. Family structure	Traditional
1.66. Marriage rate	High
1.67. Divorce rate	Low
1.68. Fertility rate	1.5 children per woman
1.69. Infant mortality rate	10/1,000 live births
1.70. Life expectancy at birth	75 years
1.71. Sex ratio	100 males per 100 females
1.72. Ethnic composition	90% Serbs, 10% others
1.73. Religion	90% Orthodox, 10% others
1.74. Education level	90% primary, 10% secondary
1.75. Employment status	50% employed, 50% unemployed
1.76. Income level	Low
1.77. Housing conditions	Basic
1.78. Access to health services	Good
1.79. Environmental quality	Good
1.80. Social stability	Good
1.81. Political system	Democratic
1.82. Legal system	Sound
1.83. Cultural life	Rich
1.84. Sports participation	High
1.85. Leisure activities	Varied
1.86. Family structure	Traditional
1.87. Marriage rate	High
1.88. Divorce rate	Low
1.89. Fertility rate	1.5 children per woman
1.90. Infant mortality rate	10/1,000 live births
1.91. Life expectancy at birth	75 years
1.92. Sex ratio	100 males per 100 females
1.93. Ethnic composition	90% Serbs, 10% others
1.94. Religion	90% Orthodox, 10% others
1.95. Education level	90% primary, 10% secondary
1.96. Employment status	50% employed, 50% unemployed
1.97. Income level	Low
1.98. Housing conditions	Basic
1.99. Access to health services	Good
1.100. Environmental quality	Good

TABLE 1	
Summary of the results of the 1990-1991 survey of the health status of the population of the Republic of Serbia	
1. General characteristics of the population	
1.1. Total population	10,000,000
1.2. Population aged 15 years and over	7,500,000
1.3. Population aged 65 years and over	1,500,000
1.4. Population aged 75 years and over	500,000
1.5. Population aged 85 years and over	100,000
1.6. Population aged 95 years and over	10,000
1.7. Population aged 100 years and over	1,000
1.8. Population aged 110 years and over	100
1.9. Population aged 120 years and over	10
1.10. Population aged 130 years and over	1
1.11. Population aged 140 years and over	0
1.12. Population aged 150 years and over	0
1.13. Population aged 160 years and over	0
1.14. Population aged 170 years and over	0
1.15. Population aged 180 years and over	0
1.16. Population aged 190 years and over	0
1.17. Population aged 200 years and over	0
1.18. Population aged 210 years and over	0
1.19. Population aged 220 years and over	0
1.20. Population aged 230 years and over	0
1.21. Population aged 240 years and over	0
1.22. Population aged 250 years and over	0
1.23. Population aged 260 years and over	0
1.24. Population aged 270 years and over	0
1.25. Population aged 280 years and over	0
1.26. Population aged 290 years and over	0
1.27. Population aged 300 years and over	0
1.28. Population aged 310 years and over	0
1.29. Population aged 320 years and over	0
1.30. Population aged 330 years and over	0
1.31. Population aged 340 years and over	0
1.32. Population aged 350 years and over	0
1.33. Population aged 360 years and over	0
1.34. Population aged 370 years and over	0
1.35. Population aged 380 years and over	0
1.36. Population aged 390 years and over	0
1.37. Population aged 400 years and over	0
1.38. Population aged 410 years and over	0
1.39. Population aged 420 years and over	0
1.40. Population aged 430 years and over	0
1.41. Population aged 440 years and over	0
1.42. Population aged 450 years and over	0
1.43. Population aged 460 years and over	0
1.44. Population aged 470 years and over	0
1.45. Population aged 480 years and over	0
1.46. Population aged 490 years and over	0
1.47. Population aged 500 years and over	0
1.48. Population aged 510 years and over	0
1.49. Population aged 520 years and over	0
1.50. Population aged 530 years and over	0
1.51. Population aged 540 years and over	0
1.52. Population aged 550 years and over	0
1.53. Population aged 560 years and over	0
1.54. Population aged 570 years and over	0
1.55. Population aged 580 years and over	0
1.56. Population aged 590 years and over	0
1.57. Population aged 600 years and over	0
1.58. Population aged 610 years and over	0
1.59. Population aged 620 years and over	0
1.60. Population aged 630 years and over	0
1.61. Population aged 640 years and over	0
1.62. Population aged 650 years and over	0
1.63. Population aged 660 years and over	0
1.64. Population aged 670 years and over	0
1.65. Population aged 680 years and over	0
1.66. Population aged 690 years and over	0
1.67. Population aged 700 years and over	0
1.68. Population aged 710 years and over	0
1.69. Population aged 720 years and over	0
1.70. Population aged 730 years and over	0
1.71. Population aged 740 years and over	0
1.72. Population aged 750 years and over	0
1.73. Population aged 760 years and over	0
1.74. Population aged 770 years and over	0
1.75. Population aged 780 years and over	0
1.76. Population aged 790 years and over	0
1.77. Population aged 800 years and over	0
1.78. Population aged 810 years and over	0
1.79. Population aged 820 years and over	0
1.80. Population aged 830 years and over	0
1.81. Population aged 840 years and over	0
1.82. Population aged 850 years and over	0
1.83. Population aged 860 years and over	0
1.84. Population aged 870 years and over	0
1.85. Population aged 880 years and over	0
1.86. Population aged 890 years and over	0
1.87. Population aged 900 years and over	0
1.88. Population aged 910 years and over	0
1.89. Population aged 920 years and over	0
1.90. Population aged 930 years and over	0
1.91. Population aged 940 years and over	0
1.92. Population aged 950 years and over	0
1.93. Population aged 960 years and over	0
1.94. Population aged 970 years and over	0
1.95. Population aged 980 years and over	0
1.96. Population aged 990 years and over	0
1.97. Population aged 1000 years and over	0
1.98. Population aged 1010 years and over	0
1.99. Population aged 1020 years and over	0
1.100. Population aged 1030 years and over	0
1.101. Population aged 1040 years and over	0
1.102. Population aged 1050 years and over	0
1.103. Population aged 1060 years and over	0
1.104. Population aged 1070 years and over	0
1.105. Population aged 1080 years and over	0
1.106. Population aged 1090 years and over	0
1.107. Population aged 1100 years and over	0
1.108. Population aged 1110 years and over	0
1.109. Population aged 1120 years and over	0
1.110. Population aged 1130 years and over	0
1.111. Population aged 1140 years and over	0
1.112. Population aged 1150 years and over	0
1.113. Population aged 1160 years and over	0
1.114. Population aged 1170 years and over	0
1.115. Population aged 1180 years and over	0
1.116. Population aged 1190	



2. each particle occupies an area of at least 5 pixels.

In the case of some specimens, these two criteria cannot be combined for a single magnification.

5 In this case, two series of different magnifications are used.

The electron microscopy images are digitized (in order to obtain a digital representation of 512 x 512 pixels each coding 256 grey levels) and then  
10 put into binary form so that the image now comprises only points having the value 1 or the value 0, using two operations - firstly a morphology gradient operation, followed by a size-2 top hat transformation (see, on the subject Jean SERRA, "Image Analysis and  
15 Mathematical Morphology, Vol. 1, Academic Press 1982).

The binary image is then manually restored (closure of contours, disconnection of objects and  
elimination of artefacts) so as to remove artefacts such as traces due to the cutting operation, cracks in  
20 the material or juxtapositions of nodules.

When two magnifications are necessary, the series of images taken with the lowest magnification undergoes an extraction operation, namely the coarsest nodules are selected and extracted so as to appear by  
25 themselves in the final image. These images serve as the basis for measuring their size. The space left by omitting the nodules not selected will subsequently be filled virtually, using the particle size measurement

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10 FEB 80 10 30

determined by analysing the series taken with the higher magnification (see the data reconciliation procedure below).

The binary images are then analysed using a measurement module. In general, from 15 to 20 images of the same specimen are used in order to obtain representative statistics. The percentage area occupied by the sections of nodules (objects) in the matrix (background) is estimated simply by counting the number of pixels having the value 1 in the images and by adding this number to the total number of pixels in the images. The area of each of the individual objects in the image is measured and this area allows the equivalent diameter to be calculated. The concept of equivalent diameter makes it possible to get round the problem of the shape of the object:  $D_{eq}$  is the diameter of a disc which would have the same area as the object measured. Only complete objects are taken into account (partially visible nodules are eliminated, i.e. cut off by the edges of the image).

After a statistical edge-effect correction, called a Miles-Lantuejoul's correction (see, on this subject: Michel Coster & Jean-Louis Chermant, "Précis d'Analyse d'Images [*Précis of Image Analysis*]", Presses du CNRS, 1989), a frequency histogram  $n_i = f$  (equivalent diameter  $D_{eq,i}$ ) is formed.

5

where  $N_T = \sum_{i=1}^{i=\max} n_i$

10

imax being the total number of classes in the  
15 histogram (number of different values of  $D_{eq}$ ).

$$FS_k = \frac{\sum_{i=1}^{i=k} S_i}{S_T} = f(D_{eq})$$

$S_T$  being the total area occupied by the nodules taken into account (not those cut off by the edges of the image),

$n_i$  being the number of nodules in the size class defined by  $D_{eq,i}$  and

$S_i$  being the area occupied by the nodules belonging to the size class defined by  $D_{eq,i}$ ,

- 5 is very suitable for showing bimodality in the population. In fact, the distribution of particle sizes may be regarded as being bimodal if this cumulative representation has a point of inflection.

- When two magnifications have to be used to  
 10 characterize the distributed nodule populations, a procedure for combining the two sets of data coming from the separate analysis of each magnification [list of equivalent diameters] is employed (data reconciliation). This combining procedure uses the  
 15 ratio of the areas scanned in the sections in order to normalize the two populations: by taking as base the scanned area for determining the particle sizes of the coarse nodules (cumulative total of the field areas scanned at low magnification), the particle size of the  
 20 small nodules [low magnification] is used to construct a homogeneous population. The proportionality coefficient between the two populations is given by the following ratio:

$$Q = \frac{S_1 - S_{\text{nodules}}}{S_0}$$

25

where  $S_0$  and  $S_1$  are the scanned areas in the section under high magnification and under low magnification, respectively, and  $S_{\text{nodules}}$  is the area occupied by the

sections of nodules in the series of images taken at low magnification. This ratio  $Q$  is used to multiply the number of occurrence of equivalent diameters determined by analysing the series of images taken at high

5 magnification.

The histograms thus normalized are combined by choosing a cut-off threshold between the two sets of data. This threshold is chosen in an interactive manner in the region of overlap of the histograms.

10 The same calculations as previously are carried out on the resulting population, after it has been normalized.

#### EXAMPLE 1 (comparative example)

15 The following materials are introduced, at room temperature, into a 16 litre stainless steel reactor fitted with a stirring system and with a temperature controller: 9470 g of styrene, 660 g of ethylbenzene, 220 g of a plasticizing mineral oil of  
20 the brand PRIMOL 352 sold by the company Esso, 11 g of an antioxidant of the brand IRGANOX 1076 sold by the company Ciba and 640 g of a homopolybutadiene of the brand BUNA CB HX 527 SIC sold by the company Bayer, this rubber having a weight-average molar mass of  
25 245,000 g/mol, a polydispersivity index of 2.35, a 100°C (1+4) ML Mooney viscosity of 46 and a viscosity as a 5% by weight solution in styrene at 25°C of 145 mPa.s. The mixture is stirred at 80 revolutions per

minute. After completely dissolving the polybutadiene,  
2.9 g of isopropyl tert-butyl peroxy carbonate (i.e.  
 $1.235 \times 10^{-2}$  mol) diluted to 75% by weight in a  
hydrocarbon, sold under the brand LUPEROX TBIC-M75 by  
5 the company Luperox, are introduced. The solution is  
heated to 130°C in 30 minutes. This temperature is  
maintained for 1 h 30 min. and then heated to 145°C.  
The polymerization conversion is monitored by taking  
regular samples during the polymerization step and by  
10 determining the solids content on the said samples.

The term "solids content" should be  
understood to mean the percentage by weight of solids,  
obtained after evaporation under a vacuum of 25  
millibar for approximately 20 minutes at 200°C, of the  
15 samples taken with respect to the initial weight of the  
sample taken. After phase inversion, the stirring is  
reduced from 80 to 40 revolutions per minute. After a  
solids content of approximately 60% has been obtained,  
the contents of the reactor are transferred into a  
20 superheater at 230°C so as to crosslink the elastomer  
(residence time: approximately 10 minutes) and then  
into a devolatilizer at 230°C under a vacuum of about  
50 mbar so as to remove the ethylbenzene and the  
residual styrene. The properties of the composition  
25 thus obtained are given in Tables 1 and 2. Figure 1 is  
a number-based and area-based cumulative representation  
of the amounts of particles as a function of their  
equivalent diameter.

**EXAMPLE 2**

The procedure is carried out as in Example 1, except that 1.6 g (i.e.  $0.93 \times 10^{-2}$  mol) of the stable  
5 free radical 4-hydroxy-2,2,6,6-tetramethyl piperidinyloxy (which may be called OH-TEMPO) are added just before the heating step and except that the polymerization temperature is set at 120°C.

The properties of the composition thus  
10 obtained are indicated in Tables 1 and 2. Figure 2 is a number-based and area-based cumulative representation of the amounts of particles as a function of their equivalent diameter.

**EXAMPLE 3**

The procedure is carried out as in Example 2, except that just before the heating step 4.9 g of  
LUPEROX TBIC-M75 (i.e.  $2.085 \times 10^{-2}$  mol) are added  
instead of the 2.9 g. The properties of the composition  
20 thus obtained are given in Tables 1 and 2. Figure 3 is a number-based and area-based cumulative representation of the amounts of particles as a function of their equivalent diameter.

**EXAMPLE 4**

The procedure is carried out as in Example 1 except that, before the heating step, 8.75 g of LUPEROX TBIC-M75 (i.e.  $3.705 \times 10^{-2}$  mol), instead of the 2.9 g,

and 4.25 g (i.e.  $2.47 \times 10^{-2}$  mol) of OH-TEMPO are added. In addition, the polymerization temperature is set at 120°C. The properties of the compositions thus obtained are given in Tables 1 and 2. Figure 4 is a number-based and area-based cumulative representation of the amounts of particles as a function of their equivalent diameter.

#### EXAMPLE 5

The procedure is carried out as in Example 1, but by setting the polymerization temperature at 120°C and starting by initially dissolving the following ingredients in the following amounts:

- styrene: 9540 g,
- mineral oil, PRIMOL 352: 220 g,
- antioxidant, IRGANOX 1076: 11 g,
- polybutadiene of the brand BUNA CB HX 565' having a weight-average molecular mass of 172,500, a polydispersivity of 1.6, a 100°C (1+4) ML Mooney viscosity of 56 and a viscosity as a 5% by weight solution in styrene, at 25°C, of 44 mPa·s: 570 g,
- ethylbenzene: 660 g.

Just before the heating step, the following are added to the dissolution:

- LUPEROX TBIC-M75: 8.1 g, i.e.  $3.45 \times 10^{-2}$  mol,
- OH-TEMPO: 2.6 g, i.e.  $1.51 \times 10^{-2}$  mol.



The properties of the composition thus obtained are given in Tables 1 and 2. Figure 5 is a number-based and area-based cumulative representation of the amounts of particles as a function of their 5 equivalent diameter.

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TABLE 1

	UNITS	EXAMPLE No.				
		1 (comparative)	2	3	4	5
Amount of initiator (INIT)	mol	$1.235 \times 10^{-2}$	$1.235 \times 10^{-2}$	$2.085 \times 10^{-2}$	$3.705 \times 10^{-2}$	$3.45 \times 10^{-2}$
Amount of stable free radical (SFR)	mol	0	$0.93 \times 10^{-2}$	$0.93 \times 10^{-2}$	$2.47 \times 10^{-2}$	$1.51 \times 10^{-2}$
$\frac{(SFR) \times F_{SFR}}{(INIT) \times F_{INIT}}$		0	0.38	0.22	0.33	0.22
Viscosity of the polybutadiene as 5% solution in styrene at 25°C	mPa.s	145	145	145	145	44
Amount of polybutadiene (RU)	mol	$0.61 \times 10^{-2}$	$0.61 \times 10^{-2}$	$0.61 \times 10^{-2}$	$0.61 \times 10^{-2}$	$0.53 \times 10^{-2}$
$\frac{(SFR) \times F_{SFR}}{(RU)}$		0	1.5	1.5	4	2.9
Amount of polybutadiene	% by weight	8.5	8.5	8.5	8.6	8.4
Melt index MI <sub>1</sub>	g/10 min.	2.9	2.6	3.6	10.3	6.4
Izod impact strength	kJ/m <sup>2</sup>	11.6	14.1	15.4	13	5.3
Vicat softening temperature (1 kg)	°C	94.5	95.0	94.7	95	94.7
Gloss	UB	29	21	40	65	82
Transparency (haze)	%	80			75	30

TABLE 2

		EXAMPLE NO.			
1		2	3	4	5
(comparative)		monomodal	bimodal	bimodal	monomodal
Nodule distribution	% by area	49	22	47	100
	morphology	capsule + <u>salami</u>	capsule + <u>salami</u>	capsule + onion + labyrinth	capsule
Particles having an equivalent diameter of between 0.1 and 1 $\mu$ m	% by area	28	9	16	-
	morphology	salami	salami	onion + <u>labyrinth</u>	-
Particles having an equivalent diameter of greater than 1.6 $\mu$ m	% by area	23	69	37	-
	morphology	salami	salami	labyrinth	-

## CLAIMS

1. Process for the preparation of a composition comprising a vinylaromatic polymer matrix
- 5 surrounding rubber nodules, comprising a step of polymerizing at least one vinylaromatic monomer in the presence of a rubber, of a stable free radical which is not introduced into the polymerization mixture in a form linked to the rubber, and of a polymerization
- 10 initiator with a grafting character suitable for the said composition
- is such that in one of its sections at least 90% of the total area occupied by the nodules corresponds to capsules having an equivalent diameter ranging from
  - 15 0.1 to 1  $\mu\text{m}$ , or else
  - is such that it comprises multi-occlusion-type nodules and is such that in one of its sections
    - 20 to 60% of the total area occupied by the particles corresponds to particles having an equivalent
    - 20 diameter ranging from 0.1 to 1  $\mu\text{m}$ ,
    - 5 to 20% of the total area occupied by the particles corresponds to particles having an equivalent diameter ranging from 1 to 1.6  $\mu\text{m}$ , and
    - 20 to 75% of the total area occupied by the
    - 25 particles corresponds to particles having an equivalent diameter of greater than 1.6  $\mu\text{m}$ .
- the said step being such that:

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- if (SFR) represents the number of moles of stable free radical in the polymerization mixture,

- if  $F_{SFR}$  represents the functionality of the stable free radical, i.e. the number of sites on the same molecule of stable free radical having the stable free radical state,

- if (INIT) represents the number of moles of polymerization initiator in the polymerization mixture before phase inversion, and

- if  $F_{INIT}$  represents the functionality of the initiator introduced before phase inversion, i.e. the number of sites having the free radical state that each molecule of initiator is capable of generating, then:

$$0.05 < \frac{F_{SFR} \times (SFR)}{F_{INIT} \times (INIT)} < 1.$$

2. Process according to the previous claim, characterized in that

$$0.05 < \frac{F_{SFR} \times (SFR)}{F_{INIT} \times (INIT)} < 0.5.$$

3. Process according to one of the preceding claims, characterized in that, if (RU) represents the number of moles of rubber,

$$0.1 < \frac{(SFR) \times F_{SFR}}{(RU)} < 10.$$

4. Process according to one of the preceding claims, characterized in that the ratio of  $(INIT) \times F_{INIT}$  to the molar amount of vinylaromatic monomer ranges from  $1 \times 10^{-5}$  to  $1 \times 10^{-2}$ .

5 5. Process according to one of the preceding claims, characterized in that the ratio of  $(INIT) \times F_{INIT}$  to the molar amount of vinylaromatic monomer is greater than  $2 \times 10^{-4}$ .

10 6. Process according to one of the preceding claims, characterized in that the ratio of  $(INIT) \times F_{INIT}$  to the molar amount of vinylaromatic monomer is greater than  $4 \times 10^{-4}$ .

15 7. Process according to one of the preceding claims, characterized in that the ratio of  $(INIT) \times F_{INIT}$  to the molar amount of vinylaromatic monomer is greater than  $6 \times 10^{-4}$ .

20 8. Process according to one of the preceding claims, characterized in that the polymerization mixture during the step of the process comprises, per 100 parts by weight of vinylaromatic monomer, 2 to 35 parts by weight of rubber and 0 to 5 parts by weight of solvent.

25 9. Process according to one of the preceding claims, characterized in that the rubber has a weight-average molecular mass ranging from 110,000 to 350,000 and a number-average molecular mass ranging from 50,000 to 250,000, and in that the matrix of

vinylaromatic polymer has a weight-average molecular mass ranging from 90,000 to 250,000.

10. Process according to one of the preceding claims, characterized in that the rubber  
5 nodules have partially both a salami and/or labyrinth morphology and partially both an onion and/or capsule morphology.

11. Process according to one of the preceding claims, characterized in that the composition  
10 is such that, in one of its sections,

- 20 to 60% of the total area occupied by the particles corresponds to particles having an equivalent diameter ranging from 0.1 to 1  $\mu\text{m}$ ,

- 5 to 20% of the total area occupied by the  
15 particles corresponds to particles having an equivalent diameter ranging from 1 to 1.6  $\mu\text{m}$ , and

- 20 to 75% of the total area occupied by the particles corresponds to particles having an equivalent diameter of greater than 1.6  $\mu\text{m}$ .

20 12. Process according to the preceding claim, characterized in that:

- in the 0.1 to 1  $\mu\text{m}$  size range, more than 95% of the particles have the salami or capsule morphology,

25 - in the 1 to 1.6  $\mu\text{m}$  size range, more than 95% of the particles have the salami morphology, and

- in the greater than 1.6  $\mu\text{m}$  size range, more than 95% of the particles have the salami morphology.

13. Process according to Claim 11,  
characterized in that

- in the 0.1 to 1  $\mu\text{m}$  size range, more than  
95% of the particles have the capsule or onion or  
5 labyrinth morphology,
- in the 1 to 1.6  $\mu\text{m}$  size range, more than  
95% of the particles have the onion or labyrinth  
morphology, and
- in the greater than 1.6  $\mu\text{m}$  size range, more  
10 than 95% of the particles have the labyrinth  
morphology.

14. Process according to one of the  
preceding claims, characterized in that the  
distribution of the equivalent diameters of nodules is  
15 bimodal.

15. Process according to one of Claims 10 to  
14, characterized in that the rubber has, as a 5% by  
weight solution in styrene, a viscosity at 25°C ranging  
from 60 to 300 mPa.s.

20 16. Process according to one of Claims 10 to  
15, characterized in that the rubber has a weight-  
average molecular mass ranging from 175,000 to 350,000  
and a number-average molecular mass ranging from 70,000  
to 250,000.

25 17. Process according to the preceding  
claim, characterized in that the rubber has a weight-  
average molecular mass ranging from 200,000 to 300,000



and a number-average molecular mass ranging from 90,000 to 200,000.

18. Process according to one of Claims 1 to 9, characterized in that the composition is such that, in one of its sections, at least 90% of the total area occupied by the particles corresponds to capsules having an equivalent diameter ranging from 0.1 to 1  $\mu\text{m}$ .

19. Process according to the preceding claim, characterized in that the rubber has, as a 5% by weight solution in styrene, a viscosity at 25°C ranging from 15 to 60 mPa.s.

20. Process according to Claim 18 or 19, characterized in that the rubber has a weight-average molecular mass ranging from 110,000 to 200,000 and a number-average molecular mass ranging from 50,000 to 200,000.

21. Process according to the preceding claim, characterized in that the rubber has a weight-average molecular mass ranging from 150,000 to 200,000 and a number-average molecular mass ranging from 70,000 to 150,000.

22. Process according to one of the preceding claims, characterized in that the rubber is a homopolybutadiene.

23. Process according to one of the preceding claims, characterized in that the initiator is one of the following:

- isopropyl *tert*-butyl peroxycarbonate,

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- 5                   - 2-ethylhexyl tert-butyl peroxy carbonate,  
                  - dicumyl peroxide  
                  - di-tert-butyl peroxide,  
                  - 1,1-bis(tert-butylperoxy)cyclohexane,  
                  - 1,1-bis(tert-butylperoxy)-3,3,5-  
                  trimethylcyclohexane,  
                  - tert-butyl peroxyacetate,  
                  - cumyl tert-butyl peroxide,  
                  - tert-butyl perbenzoate,  
10                   - tert-butyl per-2-ethylhexanoate,  
                  - 2,2-bis(tert-butylperoxy)butane,  
                  - butyl 4,4-bis(tert-butyl)valerate,  
                  - ethyl 3,3-bis(tert-butyl)butyrate,  
                  - 2,2-bis(4,4-di-tert-butylperoxycyclo-  
15                   hexyl)propane.
24. Process according to one of the  
preceding claims, characterized in that the initiator  
is chosen from diacyl peroxides, peroxy esters, dialkyl  
peroxides and peroxy acetals.
- 20                   25. Process according to the preceding  
claim, characterized in that the initiator generates at  
least one tert-butyloxy radical.
26. Process according to the preceding  
claim, characterized in that the initiator is one of  
25                   the following:
- isopropyl tert-butyl peroxy carbonate,  
                  - 1,1-bis(tert-butylperoxy)cyclohexane,

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- 1-1-bis(*tert*-butylperoxy)-3,3,5-trimethyl-  
cyclohexane.

27. Process according to one of the  
preceding claims, characterized in that the  
5 polymerization step is carried out at least partially  
at 80 to 140°C.

28. Process according to one of the  
preceding claims, characterized in that the  
polymerization step is carried out at least partially  
10 at 90 to 130°C.

29. Process according to one of the  
preceding claims, characterized in that the  
polymerization step is carried out at least partially,  
before phase inversion, at a temperature T such that  
15  $T_g - 20^\circ\text{C} < T < T_g + 20^\circ\text{C}$ , in which  $T_g$  represents the  
temperature at which 50% of the initiator is decomposed  
in one hour.

30. Process according to the preceding  
claim, characterized in that the step is carried out at  
20 least partially at a temperature T such that  
 $T_g - 10^\circ\text{C} < T < T_g + 10^\circ\text{C}$ .

31. Process according to one of the  
preceding claims, characterized in that the  
polymerization initiator is added to the polymerization  
25 mixture after phase inversion.

32. Process according to one of the  
preceding claims, characterized in that the  
vinylaromatic monomer is styrene.

33. Process according to one of the preceding claims, characterized in that the polymerization is carried out continuously so that the phase inversion takes place in a plug-flow reactor.

5 34. Composition capable of being obtained by the process of one of the preceding claims.

35. Composition according to the preceding claim or comprising a stable free radical which is in a free form or in a form linked to a polymer chain by a covalent bond, comprising a matrix of vinylaromatic polymer surrounding rubber nodules, characterized in that the composition comprises nodules of the multi-occlusion type and is such that, in one of its sections,

15 - 20 to 60% of the total area occupied by the particles corresponds to particles having an equivalent diameter ranging from 0.1 to 1  $\mu\text{m}$ ,

- 5 to 20% of the total area occupied by the particles corresponds to particles having an equivalent diameter ranging from 1 to 1.6  $\mu\text{m}$ , and

20 - 20 to 75% of the total area occupied by the particles corresponds to particles having an equivalent diameter of greater than 1.6  $\mu\text{m}$ .

36. Composition according to the preceding claim, characterized in that:

25 - in the 0.1 to 1  $\mu\text{m}$  size range, more than 95% of the particles have the salami or capsule morphology,

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41. Case for a television or a video recorder or a computer or a printer or a fax machine produced by injection moulding a composition of one of Claims 35 to 40.

5           42. Composition according to Claim 34, characterized in that the composition is such that, in one of its sections, at least 90% of the total area occupied by the particles corresponds to capsules having an equivalent diameter ranging from 0.1 to 1  $\mu\text{m}$ .

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Number-based and 2D area-based histograms: Example 1

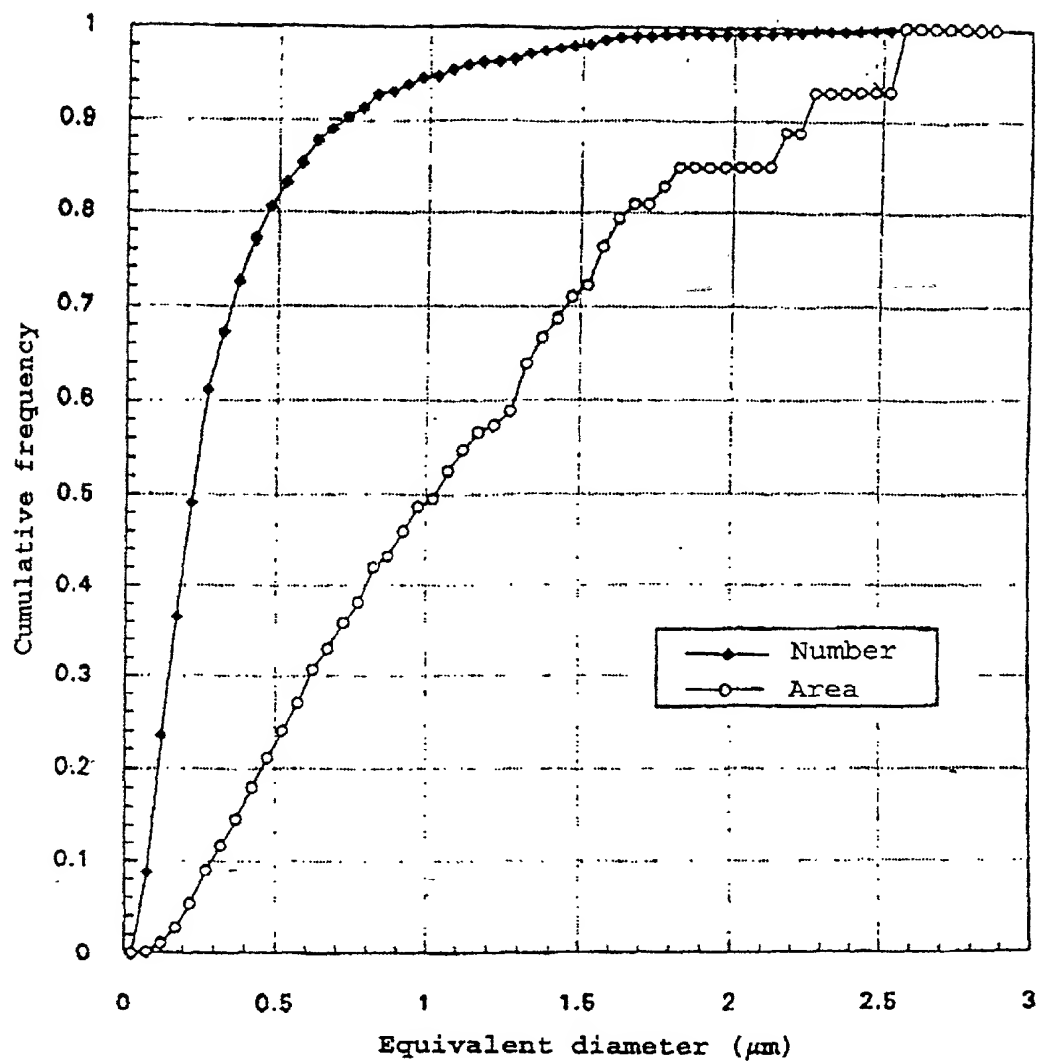


Fig 1

## Number-based and 2D area-based histograms: Example 2

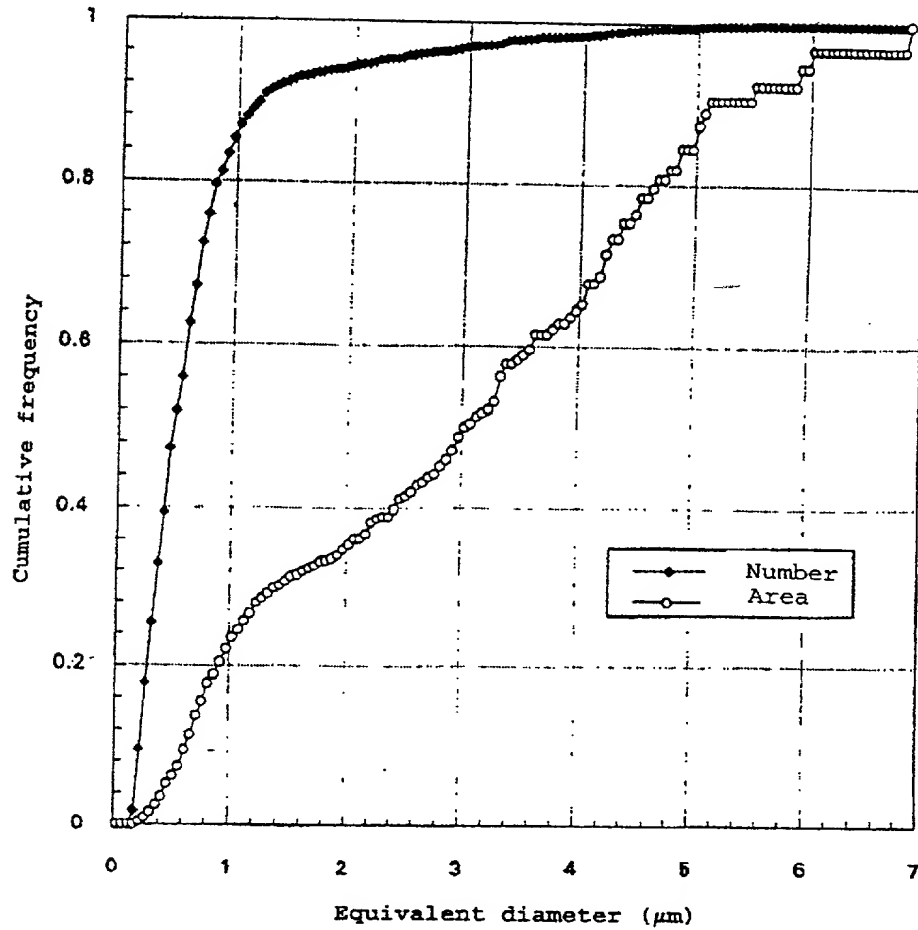


Fig 2



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## Number-based and 2D area-based histograms: Example 3

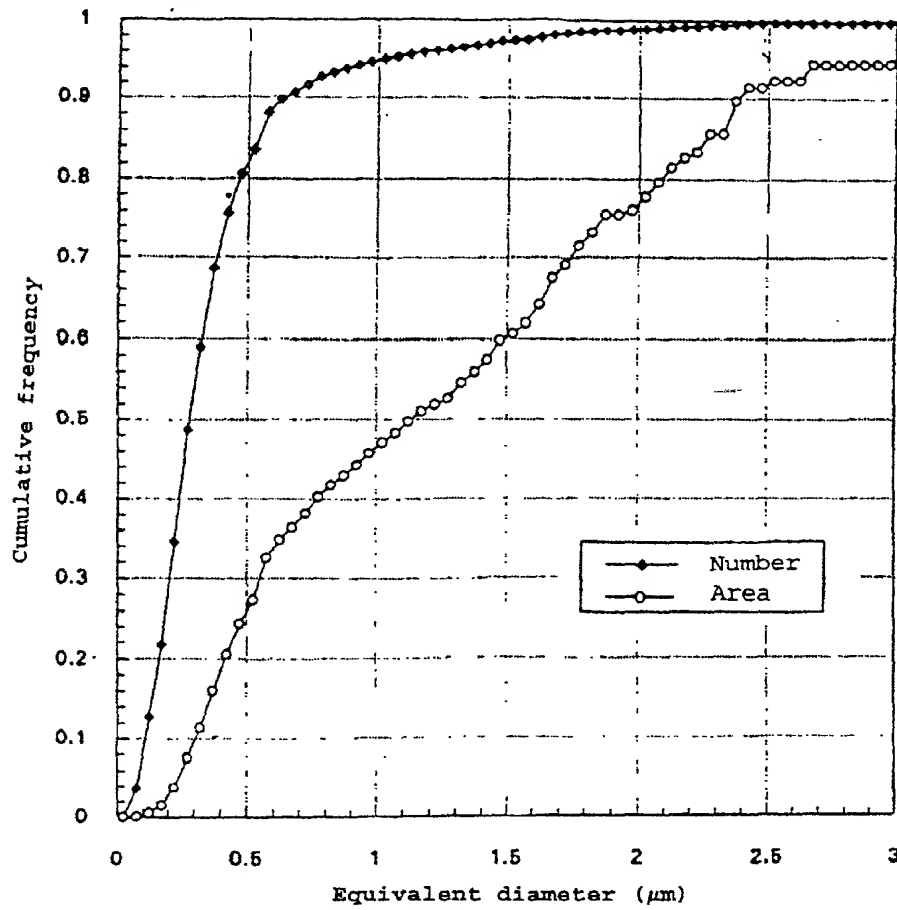


Fig 3

## Number-based and 2D area-based histograms: Example 4

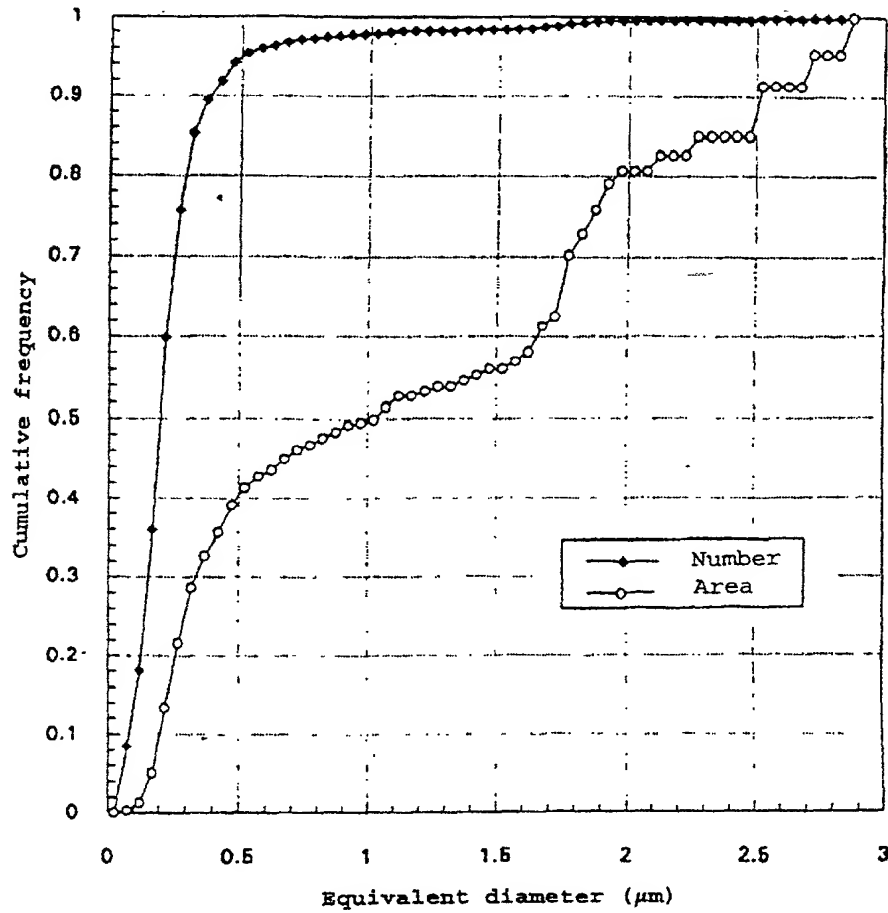


Fig 4

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## Number-based and 2D area-based histograms: Example 5

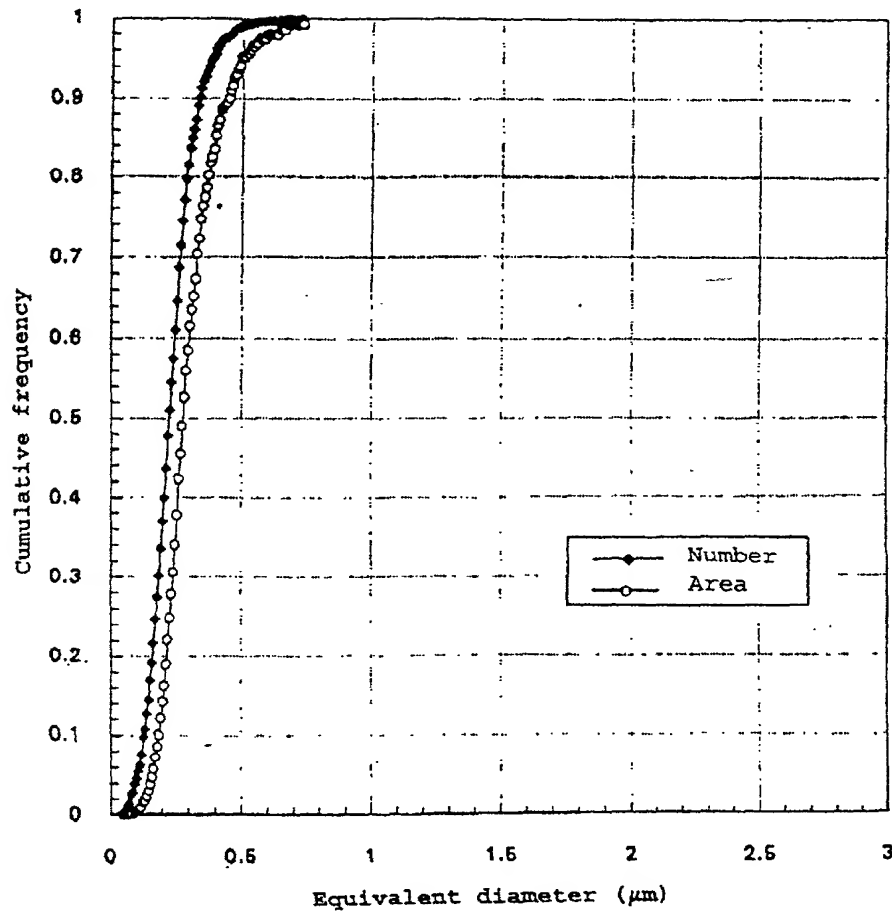


Fig 5



## DECLARATION FOR NON-PROVISIONAL PATENT APPLICATION\*

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below at 201 et seq. beneath my name.

I believe I am the original, first and sole inventor if only one name is listed at 201 below, or an original, first and joint inventor if plural names are listed at 201 et seq. below, of the subject matter which is claimed and for which a patent is sought on the invention entitled

SHOCK VINYLAROMATIC POLYMER BY POLYMERIZATION OF A VINYLAROMATIC MONOMER IN THE PRESENCE OF A STABLE FREE RADICAL AND A POLYMERISATION INITIATOR

and for which a patent application:

☒ is attached hereto and includes amendment(s) filed on (if applicable)

☐ was filed in the United States on as Application No. (for declaration not accompanying application)

with amendment(s) filed on (if applicable)

☒ was filed as PCT international Application No. PCT/FR99/01272 on May 31, 1999 and was amended under PCT Article 19 on (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified application, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119(a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

EARLIEST FOREIGN APPLICATION(S), IF ANY, FILED PRIOR TO THE FILING DATE OF THE APPLICATION			
APPLICATION NUMBER	COUNTRY	DATE OF FILING (day, month, year)	PRIORITY CLAIMED
98/06940	France	June 2, 1998	YES <input checked="" type="checkbox"/> NO <input type="checkbox"/>
			YES <input type="checkbox"/> NO <input type="checkbox"/>
			YES <input type="checkbox"/> NO <input type="checkbox"/>

I hereby claim the benefit under Title 35, United States Code, §119(e) of any United States provisional application(s) listed below.

PROVISIONAL APPLICATION NUMBER	FILING DATE

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code §112, I acknowledge the duty to disclose information known to me which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

NON-PROVISIONAL APPLICATION SERIAL NO.	FILING DATE	STATUS		
		PATENTED	PENDING	ABANDONED

\* for use only when the application is assigned to a company, partnership or other organization.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

201	FULL NAME OF INVENTOR	LAST NAME <u>Boutillier</u>	FIRST NAME <u>Jean-Marc</u>	MIDDLE NAME	
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		SIGNATURE OF INVENTOR 201 <u>X Jean-Marc BOUTILLIER</u>		DATE <u>X December 1<sup>st</sup>, 2000</u>	
202	FULL NAME OF INVENTOR	LAST NAME	FIRST NAME	MIDDLE NAME	
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		SIGNATURE OF INVENTOR 202		DATE	
203	FULL NAME OF INVENTOR	LAST NAME	FIRST NAME	MIDDLE NAME	
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
	POST OFFICE ADDRESS	STREET	CITY	STATE OR COUNTRY	ZIP CODE
		SIGNATURE OF INVENTOR 203		DATE	
204	FULL NAME OF INVENTOR	LAST NAME	FIRST NAME	MIDDLE NAME	
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
	POST OFFICE ADDRESS	STREET	CITY	STATE OR COUNTRY	ZIP CODE
		SIGNATURE OF INVENTOR 204		DATE	
205	FULL NAME OF INVENTOR	LAST NAME	FIRST NAME	MIDDLE NAME	
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
	POST OFFICE ADDRESS	STREET	CITY	STATE OR COUNTRY	ZIP CODE
		SIGNATURE OF INVENTOR 205		DATE	

J-NB  
Dec 1<sup>st</sup>,  
2000